OPTICAL PROPERTIES and PHOTOCHEMICAL BEHAVIOUR

of some NITROSO COMPOUNDS.

T H E S I S

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SAMUEL C. CARSON, B.Sc.

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CONTENTS.

		Page.
Part I.	- Historical and Theoretical	1
" II.	- Nitroso derivatives of naturally occurring compounds.	24
"III.	- The action of nitrosyl chloride on n-hexane in presence of light.	32
" IV.	- Preparation of an optically active simple nitroso compound.	68

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Optical Properties and Photochemical Behaviour of some Nitroso Compounds.

Part I. - HISTORICAL and THEORETICAL.

The problem of the production in nature, in certain cases, of one of the optically active forms of an asymmetric compound, without the corresponding antipode, is one which has been the subject of speculation ever since the discovery of optical activity in certain organic compounds and the realisation that the products of ordinary synthetic chemistry are inactive, i.e., mixtures of the two optical antipodes in exactly equal amounts.

Various investigators, in extension of the pioneer work of Pasteur and Fischer, have developed methods for producing optically active compounds from inactive starting products, by the influence of compounds which are themselves optically active (1). The problem, therefore, resolves itself into the question as to how the primary optically active compound could be formed in nature.

It was realised, by early investigators, that no hope of producing an answer to this question was to

be found in purely chemical investigations, since the chemical properties of optical antipodes are identical. The necessity, therefore, became apparent for the use of an unsymmetrical physical force as an activating agent in a chemical change which is to result in the creation of optical activity.

It is recorded that Pasteur attempted to make a liquid active by placing it in a rapidly rotating tube and that he suggested the use of magnetism to effect separation of a racemic mixture into its optical antipodes. Other investigators have carried out chemical changes under the influence of magnetic fields in the hope of obtaining optically active products, but with no success (3). P. Curie and Cotton have examined carefully the conditions which must be fulfilled by the physical force to be used in experiments of this kind.

Curie pointed out that the physical agent must possess the enantiomorphic asymmetry characteristic of living bodies. In other words, it must not be superposable on its mirror image. This condition rules out the use of either a magnetic field or rotatory movement in a liquid (4).

Cotton drew attention to the very important condition that the force employed must be an active participant in the chemical change involved (5).

Curie's condition narrows the number of suitable physical forces from which we can reasonably expect the production of an asymmetric chemical action to the following:-

1. Electric and magnetic fields superimposed with their lines of force parallel.
2. Light rays propagated parallel to the lines of force of a magnetic field.
3. Circularly polarised light (6).

No success has, so far, been attained by the use of the first two agents.

CIRCULARLY POLARISED LIGHT as an ASYMMETRIC FORCE in the PRODUCTION of OPTICAL ACTIVITY.

Fresnel, in the course of his research on the polarisation of light, discovered that when a beam of plane polarised light enters a transparent optically active medium it is decomposed into two opposite circularly polarised beams of the same amplitude but travelling with different speeds. Owing to this difference in speed a phase difference is set up so that when the beams recombine, on leaving the medium, to give a plane polarised beam, the plane of polarisation of the original beam has been rotated through an angle.

In the case of a non-transparent optically active medium the two circularly polarised beams may be absorbed to different extents, (circular dichroism) resulting, on recombination, in the production of an elliptically polarised beam.

This latter case was first discovered and investigated by Cotton (8). With a solution of potassium dichromate and potassium tartrate Cotton found that the resulting ellipticity (i.e., the ratio of the minor to the major axis of the elliptically polarised beam) varied with wave length, rising to a maximum at the head of the absorption band while the rotation of the solution showed a maximum on the long wave side and fell to zero at the head. This variation of ellipticity and rotation within a region of absorption is called the Cotton Effect.

The property of circular dichroism in the active form of a photo-sensitive compound leads to the possibility of the use of circularly polarised light for the production of optical activity from the racemic mixture of such a compound. The antipodes of a mixture of this kind absorb different amounts of say left-handed circularly polarised light, so that on illumination with this type of light, provided a photochemical change

takes place, one form of the compound will be destroyed more rapidly than the other, resulting in the production of optical activity. This optical activity is the result of an asymmetric photo-chemical decomposition. Similarly, optical activity may be produced by the preferential formation of the product of the photochemical action if it is potentially optically active. This optical activity is the result of an asymmetric photochemical synthesis*. An asymmetric photochemical synthesis will always be accompanied by an asymmetric photochemical decomposition. This question will be fully discussed later.

The production of optical activity by means of circularly polarised light was first suggested by van't Hoff in 1894 (9), and the natural significance of the use of this particular agent was demonstrated by Byk (10), who showed that an excess of circularly polarised light of one sign (right) is present on the surface of the earth.

Since the time of van't Hoff, numerous investigators have worked along these lines but only in

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*This is not a true asymmetric synthesis according to the strict definition of Marckwald (34). However, for convenience, the term will be used throughout this thesis in the sense indicated above.

comparatively recent years has success been attained. A list of positive results is given below, where the rotation produced was of such a magnitude as to make the success of the experiment beyond doubt.

(1) Kuhn and Braun. (11).

These authors irradiated an alcoholic solution of the inactive ethyl ether of α-bromo propionic acid with circularly polarised light of wave length about 2800A. After destruction of about 50% of the compound it was found that the solutions exposed to left-handed circularly polarised light had developed a laevo rotation and conversely. The magnitude of the rotation observed was 0.05^{o}, but it vanished on standing. This successful experiment was preceded by an examination of the rotatory dispersion and absorption of the active form of the compound, although the circular dichroism was not measured. The active form of the compound shows a Cotton Effect within the region of wave lengths which were used to effect the photochemical decomposition.

(2) Kuhn and Knopf. (12).

The starting product in this case was the dimethylamide of α-azido propionic acid. The absorption band concerned is a feeble one with its head at 2900A and is associated with the azido (N_3) grouping. The

rotatory dispersion and circular dichroism of the active form was examined and the degree of circular dichroism found to be fairly high. Also the quantum yield for the photochemical action was measured and found to be approximately unity. The importance of this factor will be discussed later.

After 36% decomposition of the compound with left and right-handed circularly polarised light, the rotation developed was in one case -1.04°, and in the other +0.78°. These rotations did not change on standing. This optical activity is definitely due to an asymmetric photochemical decomposition since it has been shown that none of the photochemical decomposition products of the compound in question are potentially optically active.

(3) Mitchell. (13).

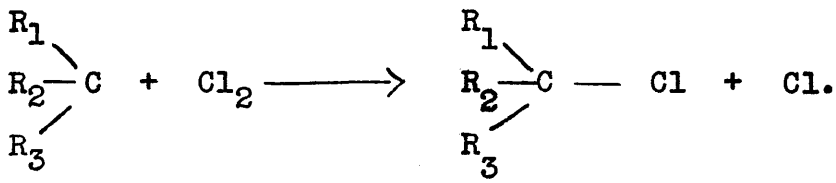
Mitchell examined the rotation dispersion and circular dichroism of caryophyllene nitrosite and found a Cotton Effect within the region of absorption in the red. Since the racemic form of caryophyllene is not known, the nitrosite of an analogous compound, humulene, was used for the asymmetric decomposition.

The rotations developed by left and right-handed circularly polarised light were measured at regular

intervals of time and graphs drawn, plotting rotation developed against time of illumination. A remarkable agreement between the two curves was found. The highest rotation produced from a 7% solution of the nitrosite was 0.30° for the mercury yellow line and 0.21° for mercury green.

(4) Karagunis and Drikos. (14).

These authors succeeded in producing an optically active compound by the influence of circularly polarised light on the addition of chlorine to triaryl carbon compounds, thus:-



The maximum rotation produced was 0.15°. This rotation is very probably due entirely to an asymmetric photochemical synthesis since there is some evidence that any activity due to the triaryl carbon compound left behind would be destroyed by racemisation.

Below is given a list of the properties required by a compound which is to be used for asymmetric photochemical work. It should be noted that in each case of the above successful experiments these conditions are fulfilled by the compounds used.

1. The compound must be a racemic mixture. Thus, in general, it must contain an asymmetric carbon atom.

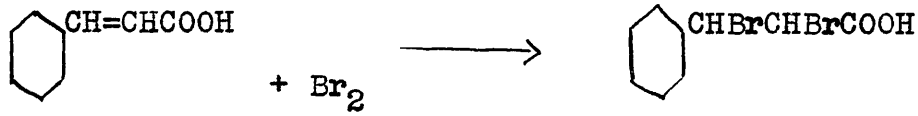
This condition is obvious since there must be two forms of the compound present to react differently towards the circularly polarised light used. In the case of the compounds used by Karagunis and Drikos, this condition was uncertain, but the success of the experiment placed it beyond doubt. In fact, the object of this particular attempt to produce optical activity was to show that the starting product was potentially optically active.

2. The active form of the compound must show circular dichroism. In other words, it must show a Cotton Effect within some spectral region.

3. The compound must undergo some chemical change under the influence of the wave lengths of light for which the active form exhibits its circular dichroism.

Several outstanding attempts at the production of optical activity by the method indicated were doomed to failure because one or other of these three conditions was not fulfilled, e.g., Cotton attempted an asymmetric decomposition of alkaline solutions of copper racemate (15). Conditions 2 and 3 are not satisfied in this case, since Byk (16) has shown that the solutions are not acted upon by light from the red end of the spectrum, for which they exhibit circular dichroism and also

Mitchell (17) has demonstrated that solutions of the active copper salt do not show circular dichroism for the photochemically active wave lengths of light. Again, Cherbuliez (18) attempted to produce an optically active compound by the influence of circularly polarised light on the bromination of cinnamic acid, thus:-



Here condition 1 is not satisfied and hence also condition 2.

A recent attempt which is very similar to that of Cherbuliez should be mentioned here. Davis and Heggie (19) report the production of optical activity by the influence of circularly polarised light on the bromination of trinitrostilbene. The photochemical action is a simple addition of bromine to a compound which does not contain an asymmetric carbon atom, and so condition 1 is apparently not satisfied. The authors, however, deduce that the positive result of their experiment indicates that "the ethylenic linkage of trinitrostilbene is by no means the rigid structure conceived by van't Hoff and suggests that it is in some manner potentially asymmetric." The rotation

developed was of the order of 0.04°. This figure, however, is too small to be conclusive and does not justify further speculation on the point.

Besides confirmation to the three primary conditions there are several other factors which play an important part in successful asymmetric photochemical work. These factors are summarised briefly below.

a) The specific rotation of the active form of the starting product should be high.

b) The degree of circular dichroism of the active form should be great. This is usually expressed as the anistropy factor, 'g', where $g = \frac{\varepsilon_l - \varepsilon_r}{\varepsilon}$

ε_l = the coefficient of absorption of one of the active forms for left-handed circularly polarised light.

ε_r = the coefficient of absorption of the same form for right-handed circularly polarised light.

$$\varepsilon = \frac{\varepsilon_l + \varepsilon_r}{2}.$$

c) Einstein's law of photochemical equivalence should be approximately obeyed for the photochemical action. In other words, for every quantum of energy absorbed one molecule only of the compound should be destroyed. In a photochemical reaction in which more than one molecule is decomposed by one quantum of light

energy a molecule of the 'd' form, say, may be activated and instead of being destroyed thereon it may react with a second molecule. This secondary reaction is non-selective, i.e., the probability of an activated 'd' molecule attacking another 'd' molecule is the same as the probability of it attacking an 'l' molecule, when 'd' and 'l' forms are present in equal quantity. This results therefore in a decrease in the efficiency of the circularly polarised light; but, more important, as the original compound is removed selectively and the residue becomes richer in, say, the 'd' form, then the probability of destruction of 'd' molecules in the secondary reaction is increased. This effect will, of course, reduce the rotation developed.

This result is perfectly general, no matter what mechanism gives rise to the increase in the quantum yield.

Kuhn (20) has derived a formula to predict the value of the rotation to be expected by the decomposition of a racemic mixture with circularly polarised light, assuming that Einstein's law holds for the photochemical action, thus

$$\alpha' = \alpha^{3/2}(1-\beta)\log\frac{1}{1-\beta}$$

α' = the rotation developed from a solution containing the 'dl' mixture.

α = the rotation of a solution of the pure 'd' or 'l' compound of concentration equal to that of the 'dl' solution used.

g = the anistropy factor.

β = the degree of decomposition.

Thus for a fixed degree of decomposition $\alpha' \propto \alpha g$. From this relation the importance of conditions 'a' and 'b' will be seen.

d) It has already been mentioned that an asymmetric photochemical synthesis is always accompanied by a similar decomposition. The rotation due to such a synthesis may oppose that due to the decomposition, thus reducing the resulting effect. The converse, of course, may occur, with a large resulting effect. However, it is often impossible to predict the signs of rotations produced in this manner and so it is apparent that there will be a greater chance of success if experiments of this kind are restricted to simple asymmetric photochemical decompositions where the centre of asymmetry of the compound is destroyed by the action of light. Such a restriction would also simplify interpretation of results.

Much of the work described in this thesis deals with photochemical actions which seemed likely to conform to this particular restriction.

For these investigations compounds containing the nitroso grouping were used.

Nitroso Compounds.

Nitroso compounds, from the point of view of asymmetric photochemical work, fall into the following two groups:-

A. Nitroso derivatives of naturally occurring compounds.

B. Simple aliphatic nitroso compounds.

Such nitroso compounds are generally blue, in the mono-molecular form, with a narrow absorption band in the red, and in many cases they are acted upon by light of wave lengths within the band.

A. Nitroso derivatives of naturally occurring compounds.

Mitchell (13), as previously described, has investigated the nitrosites of caryophyllene and humulene. Caryophyllene nitrosite exhibits circular dichroism and anomalous rotatory dispersion (The Cotton Effect) within the region of the absorption band in the red, and with humulene nitrosite a successful asymmetric photochemical decomposition was carried out.

Later Mitchell and Cormack (22) examined the nitrosites of Zingiberine, Phellandrene and Bornylene. The first two compounds were found to be too unstable

for measurement of rotatory dispersion but with Bornylene nitrosite some very interesting results were obtained. This compound dissolves to give colourless solutions at ordinary temperatures, which give normal rotatory dispersion, but on warming a blue colour is developed accompanied by a Cotton Effect*. This phenomenon is the result of the bi-molecular (colourless) form of the nitrosite splitting down into the monomolecular (blue) form.

These results made it desirable to extend this line of research and so several analogous nitroso derivatives of naturally occurring compounds were examined to see if they were suitable for asymmetric photochemical work. The following were the compounds examined:-

1. Santene nitrosite.
2. α-Pinene nitrosochloride.
3. Bis nitroso l-menthone.

Difficulty in obtaining a reasonable quantity of the naturally occurring Santene ruled out the first compound while the other two compounds were found to be too unstable for this work.

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*The highest observed anisotropy factor is recorded for these solutions.

In the case of bis nitroso l-menthone, however, it was found possible to take some measurements of rotation-dispersion. This compound, like Bornylene nitrosite, gives a normal rotatory dispersion curve at ordinary temperatures and, while accurate measurements were found to be impossible, an anomaly in the dispersion curve at the red end of the spectrum was detected, on warming.

The investigation of these compounds is described in Part II.

B. Simple nitroso compounds.

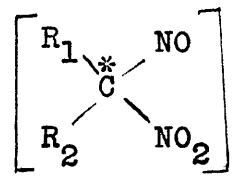
The nitroso derivatives of naturally occurring compounds are convenient for investigation from the point of view of asymmetric photochemical work; principally on account of the fact that they may be obtained in the optically active form if the naturally occurring compound is active and so measurements of optical rotation and circular dichroism may be made. This field of compounds has, however, become almost exhausted and so it was decided to carry out an examination of some simple nitroso compounds to see if they are suitable for this work (cf. conditions previously enumerated).

First of all, nitroso compounds with the nitroso group attached to an asymmetric carbon were examined

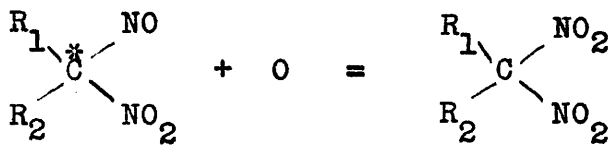
from the photochemical viewpoint. That is to say, a search was made for a simple nitroso compound which is decomposed by light with destruction of the asymmetric centre of the compound.

Secondly, a method for preparation of an optically active simple nitroso compound was sought. The object of this was to find out the magnitude of the rotation and circular dichroism associated with such simple nitroso compounds. Simple nitroso compounds from these considerations may be classified into the following groups:-

1. Pseudo nitrols.
2. Secondary nitroso compounds.
3. Tertiary nitroso compounds.

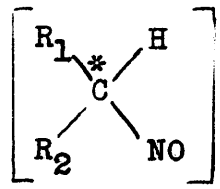
1. <u>Pseudo nitrols.</u> 

The chief importance of this class of compounds lies in the following change which takes place under the influence of light, in many cases -

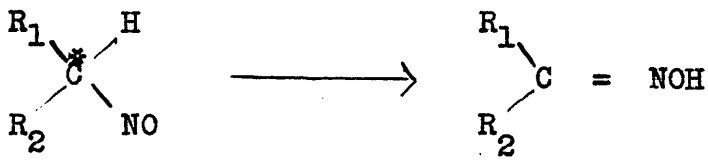


This change, of course, results in destruction of the centre of asymmetry of the compound.

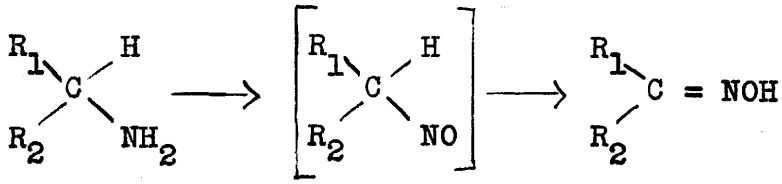
An investigation of pseudo nitrols from the point of view of asymmetric photochemical work, including an unsuccessful attempt to prepare a simple optically active member of this class of compounds, was carried out in these laboratories concurrently with this work (23).

2. Secondary nitroso compounds. 

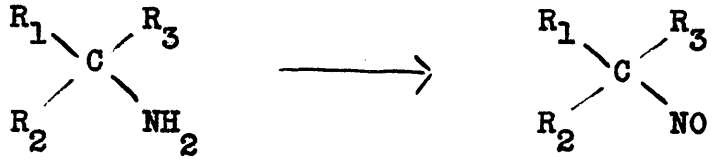
Very few examples of this type of compound are known. The reason lies in the ease with which such compounds change over to the corresponding oximes, thus -



In fact, it is generally impossible to prepare secondary nitroso compounds by the ordinary methods, presumably on account of this change over. E.g., by oxidation of secondary alkylamines with Caro's acid, oximes result -



whereas similar oxidation of tertiary alkylamines yield tertiary nitroso compounds -



(24).

However, there are a few exceptions and two of these, Monochloronitrosoethane and Trimethylethylene nitrosite were examined.

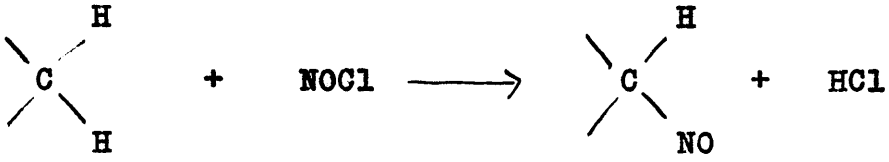
In the first case it is known that by the influence of heat or by solvent effect, the change over to the oxime takes place.

(25).

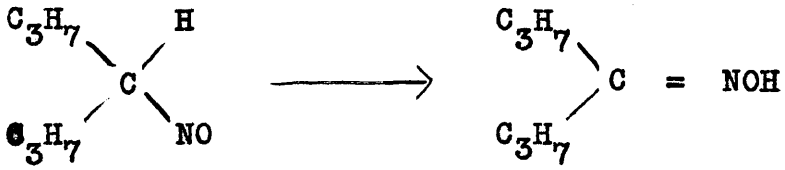
This change over results in destruction of the asymmetric centre of the compound and it was considered possible that the same change would take place under the influence of the red light absorbed by the compound. However, in both cases considered, it was found that light had little or no effect on the change in question. (See Part III of this Thesis).

An apparently general method for the production of secondary nitroso compounds was next considered. This method is due to Lynn (26) and involves the replacement of a hydrogen atom in a paraffin hydrocarbon with

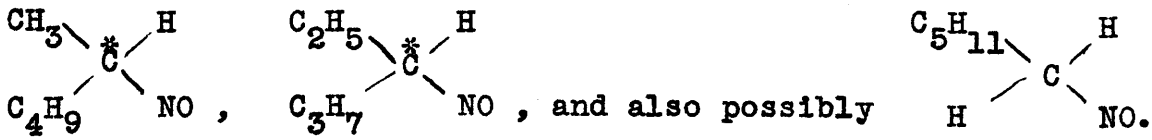
the nitroso group from nitrosyl chloride[†], by the influence of sunlight, thus:-



Lynn claimed the production of blue secondary nitroso derivatives of n-heptane[††], principally δ-nitroso heptane, and furthermore indicated that these blue compounds were changed over to the corresponding oximes, by the influence of light, thus:-



By analogy (with the above) n-hexane might be expected to give the following compounds:-



The first two compounds, β and γ nitrosohexanes, contain asymmetric carbon atoms, and the asymmetric

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[†] It is of interest to point out that Tilden in 1874 undertook an investigation, with the same end in view, but with no success (27).

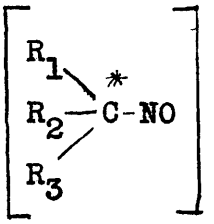
[††] Lynn did not isolate the nitroso compounds from the blue heptane solution.

centres of these compounds will be destroyed by the influence of light, if Lynn's theory concerning the action is correct.

The photochemical action of nitrosyl chloride on paraffins, apart from asymmetric photochemical considerations, is of considerable interest since it is one of the very few reactions for paraffins. Lynn's results, however, are by no means conclusive and so an investigation into the reaction, discovered by this author, was carried out.

As a result of this investigation it has been shown that the blue colour which Lynn attributed to secondary nitroso compounds is in reality due to tertiary chloronitroso compounds, and for the special case involving n-hexane an examination of the reaction has been carried out in detail.

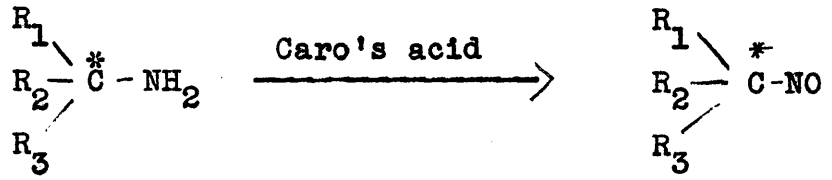
A full account of this work is given in Part III of this Thesis.

3. Tertiary nitroso compounds. 

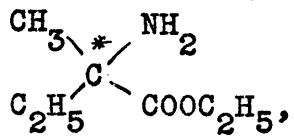
As has already been pointed out, it is important, if simple nitroso compounds are to be used in asymmetric photochemical work, that the magnitude of the rotation and degree of circular dichroism, associated with these

compounds, be known. It is necessary, therefore, that a simple optically active nitroso compound be prepared.

From consideration of the general methods for preparation of nitroso compounds the following method appeared to be the only one suitable for accomplishing this end:-

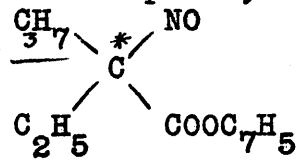


For such a preparation of an optically active simple tertiary nitroso compound it is first necessary to obtain an optically active simple tertiary alkylamine.

The tertiary alkylamine selected was ethyl ∝-methyl-∝-amino-n-butyrate  , principally on account of the fact that ∝-methyl-∝-amino-n-butyric acid, isovalin, may be resolved readily.

The preparation of the active ester of isovalin has not been carried out before and some difficulty was anticipated here, since, when attempts were made by Fischer (28) and Gadamer (29) to prepare other simple derivatives of this active amino acid, the products proved to be inactive.

However, it was found possible to prepare the active ester by the ordinary method and from it the

active nitroso compound, ethyl α-methyl-α-nitroso-n-butyrate,  .

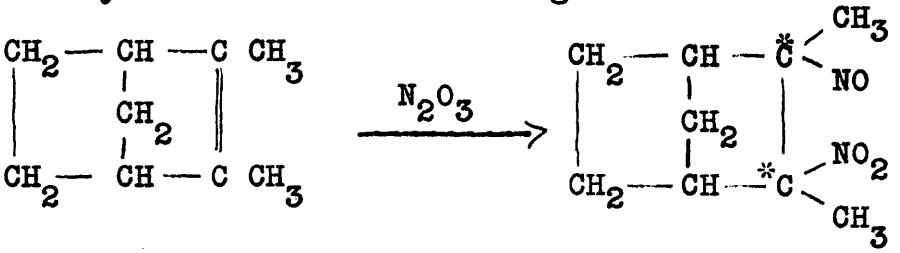
The specific rotation of the nitroso compound was of the same order as the parent amino acid and its ester, while the circular dichroism proved to be too small to measure, although a slight anomaly in the rotation-dispersion curve was detected.

This successful preparation of an optically active simple nitroso compound is described in Part IV.

Part II. NITROSO DERIVATIVES of NATURALLY OCCURRING COMPOUNDS.

1. Santene nitrosite, ($C_9H_{14}N_2O_3$).

Santene nitrosite is a blue solid and is prepared by the action of nitrous gases on santene.



The compound has two centres of asymmetry but prepared by the above method it will be inactive. It is acted upon by light and a white solid of composition $C_9H_{14}N_2O_4$ has been isolated from the products of the reaction. No further information concerning the photochemical action is available (2).

It was decided to prepare some santene nitrosite with a view to attempting an asymmetric decomposition with circularly polarised light, in a similar manner to that carried out with humulene nitrosite (13).

For the preparation it was first necessary to obtain a quantity of santene. Attempts have previously been made, in these laboratories, to isolate santene from various samples of East Indian sandalwood oil, but with no success.

Another source of santene is oil of Siberian fir, a product of the distillation of cones from Abies Siberica (7). This oil, in the crude form, is not on the market to-day. However, a refined oil of Siberian fir, commercially called Oleum Abietis, is available and several samples were obtained.

From the best sample, by fractional distillation, about 0.2% of a santene containing fraction (B.P. 135 - 150°) was obtained and from it about 2% santene was isolated in the form of the nitrosite, M.P. 116° on recrystallisation from petroleum ether.

This small percentage of santene made it impracticable to pursue the matter further.

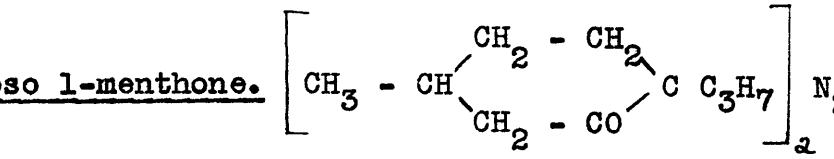
2. <u>α-Pinene nitrosochloride</u> ($C_{10}H_{16}N\ O\ Cl$).

The active form of α-Pinene nitrosochloride has been prepared by Lynn (21). The specific rotation given is $[\alpha]_D = \pm 340°$. The substance is said to form blue solutions and it is decomposed by light. Also the inactive form is easily obtained. From these considerations it appeared to be a suitable substance for examination from the point of view of asymmetric photochemical work.

A quantity of the inactive form was made by the addition of 10 c.c. concentrated hydrochloric acid to a

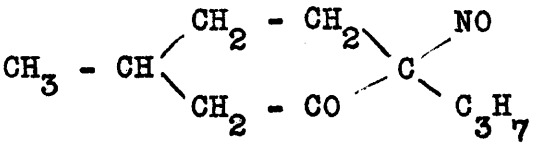
cooled mixture of equal weights (33 g.) of dl ∝-pinene, glacial acetic acid and secondary butyl nitrite. The white solid which separated was filtered off and re-crystallised from chloroform by the addition of methyl alcohol. It melted at 101.5° to give a red liquid (21).

The compound dissolved in various solvents to give slightly blue solutions. The faint blue solution in toluene was deepened in colour on warming, became faint green on cooling and green on re-warming. Solutions of toluene were kept at constant temperature (25° and 35°) in the dark but changed to a yellow colour in twenty minutes. At room temperature the solution changed to faint green in twenty minutes. This compound is too unstable for further work.

3. Bis nitroso l-menthone. 

This substance is a white solid and according to Baeyer and Manasse (30) "it could be crystallised at room temperature under 50° from alcohol, benzene and toluene. If one heats it above this temperature the solution becomes coloured through decomposition, first blue then green." From this description it was deduced that by the influence of heat the bis nitroso compound is

first of all split down into the simple nitroso compound,



in an analogous manner to Bornylene nitrosite, which exists in the form of double molecules, giving colourless solutions at ordinary temperatures, these double molecules being split up into single molecules on warming, giving blue solutions. In view of this analogy with Bornylene nitrosite it was decided to prepare a quantity of bis nitroso l-menthone and if the compound is optically active to investigate the rotatory dispersion of solutions at ordinary temperatures and also of solutions, which have developed a blue colour by warming.

Preparation of bis nitroso l-menthone.

A quantity of optically pure l-menthone $[\alpha]_{5461}$ -32.09° was obtained by oxidation of l-menthol $[\alpha]_{5461}$ -59.0°, with chromic acid. 20 gm. l-menthone was mixed with 15 g. amyl nitrite and cooled in a freezing mixture. 1.5 g. acetyl chloride was added over a period of four hours, with mechanical stirring. The liquid became green and on standing overnight deposited a mass of crystals. Ice was then added, the mixture shaken up for a short time with dilute caustic soda solution

and then filtered. The pasty mass resulting was washed with water then mixed with methyl alcohol and allowed to stand for several hours. After filtering, the white solid was recrystallised from absolute alcohol and gave M.P. 111.5° (30). The solid dissolved in benzene to give a colourless solution which on warming to about 70° became blue. On cooling slowly the blue colour disappeared at about 55°.

Rotation of bis nitroso l-menthone.

A solution of 0.1020 g. of the compound in 10 c.c. benzene gave a rotation of +1.89° for mercury green light, l = 0.6 decimetre, temperature = 18°. This gives $[\alpha]_{5461}$ +310°. The rotation decreased slowly on standing, probably due to racemisation. After the lapse of 2½ hours the rotation of the above solution had fallen to +1.75° and after standing for four days in the dark the rotation had decreased by approximately 50%. This diminution of rotation on standing is, however, not great enough to prevent constant results being obtained from measurements at ordinary temperatures.

Rotation-dispersion of bis nitroso l-menthone.

a) At ordinary temperatures.

The results of measurement of the rotation

dispersion of a solution of 0.2008 g. of the compound made up to 10 c.c. with benzene, at a temperature of 22°, are given in Table (1).

λ = wave length in Angstrom units.

α = angle of rotation for a length of 0.6 decimetre.

A graph was drawn plotting α against λ. From the resulting curve (Graph No.1) it is evident that the rotation dispersion of bis nitroso l-menthone is perfectly normal, for wave lengths within the visible spectrum, at ordinary temperatures.

b) <u>On warming.</u>

The apparatus for measurement of rotation at higher temperatures was the same as that used by Mitchell and Cormack for their work on Bornylene nitrosite (22).

The results of measurement of the rotation dispersion, at a temperature of 48°, of a solution of 0.1934 g. of bis nitroso l-menthone in 10 c.c. benzene, are given in Table (2).

α is the angle of rotation, for a length of 0.6 decimetre, measured as soon as the temperature was constant at 48°.

α' is the angle taken immediately after the first set of measurements.

Graph No.2 shows α plotted against λ (Curve 1) and also α' plotted against λ (Curve 2).

Table (1).

Rotation-Dispersion of Bis nitroso l-menthone at 22°.

λ	α
4600	+5.52°
5000	+4.41°
5200	+3.89°
5400	+3.46°
5600	+3.12°
5800	+2.76°
6000	+2.43°
6200	+2.17°
6400	+2.00°
6600	+1.87°

Graph No.1.

Rotation-Dispersion of Bis nitroso l-menthone

Temperature 22°.

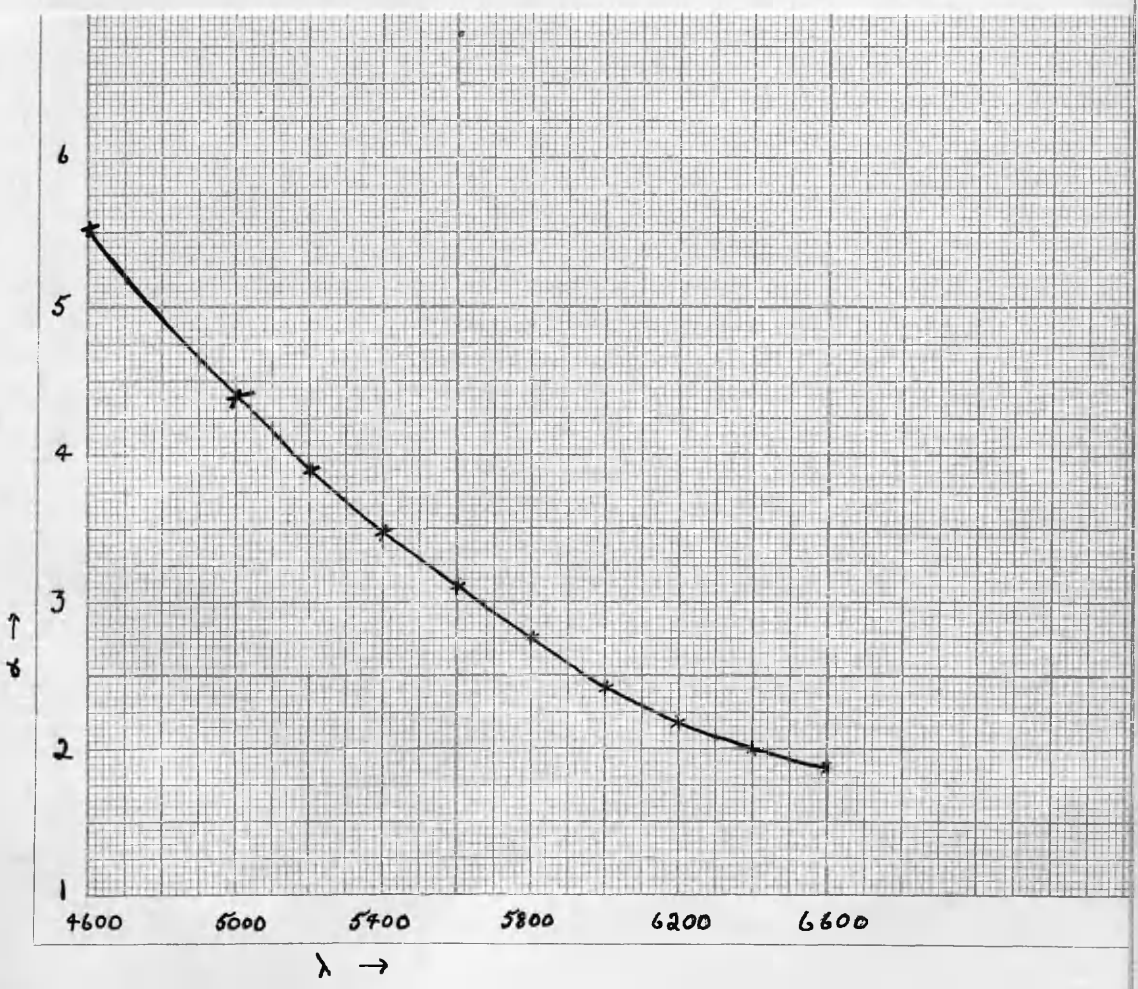


Table (2).

Rotation-Dispersion of Bis nitroso l-menthone at 48°.

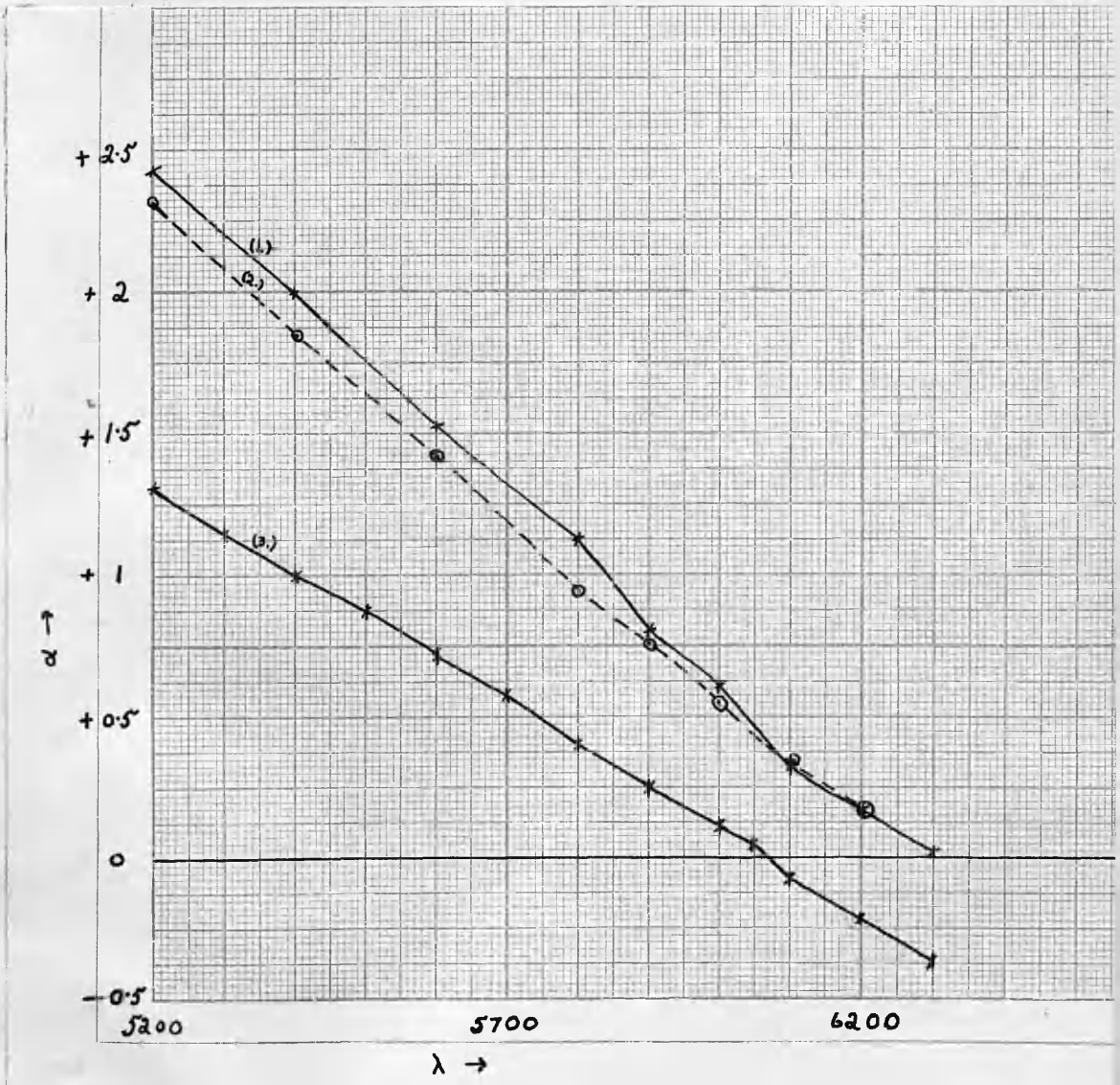
λ	α	α'
5200	+2.43°	+2.31°
5400	+1.99°	+1.84°
5600	+1.53°	+1.42°
5800	+1.12°	+0.94°
5900	+0.80°	+0.76°
6000	+0.61°	+0.55°
6100	+0.31°	+0.34°
6200	+0.17°	+0.16°
6300	+0.02°	—

Graph No.2.

Rotation-Dispersion of Bis nitroso l-menthone.

(1) and (2) - Temperature 48°.

(3) - Temperature 58°.



The solution used in the above experiment was then warmed up to 58°. The results of rotation measurements at this temperature are given in Table (3) and are represented graphically in Curve 3, Graph No.2.

From these results it is evident that accurate measurements of rotation dispersion at these higher temperatures is impossible owing to the rapid diminution of the rotation of the compound with time. However, the change of sign at approximately 6000A seemed to indicate a Cotton Effect. To confirm this change of sign a fresh solution of the same concentration as before was warmed rapidly up to 56° and measurements of rotation dispersion taken. Table (4) gives the results obtained. These results are represented in Curve (1), α plotted against λ, and Curve (2), α' plotted against λ, in Graph No.3.

The reversal of sign is thus confirmed. This reversal of sign gives rise to a very definite increase in negative rotation with wave length (anomalous dispersion) in the region 6100A - 6300A, the highest (negative) rotation observed being $[\alpha]_{6300A}$ -42°. Ellipticity measurements were attempted with the last solution at 56°. A small amount of ellipticity was detected in the region 6100A - 6300A but, owing to rapid diminution, it could not be measured with any degree of accuracy.

Table (3).

Rotation-Dispersion of Bis nitroso l-menthone at 58°.

λ	α	α'
5200	+1.31°	—
5300	+1.15°	—
5400	+1.00°	—
5500	+0.87°	—
5600	+0.72°	—
5700	+0.57°	—
5800	+0.40°	—
5900	+0.24°	—
6000	+0.11°	—
6050	+0.05°	—
6100	-0.07°	-0.04°
6200	-0.21°	-0.17°
6300	-0.38°	-0.28°
6400	—	-0.32°

Table (4).

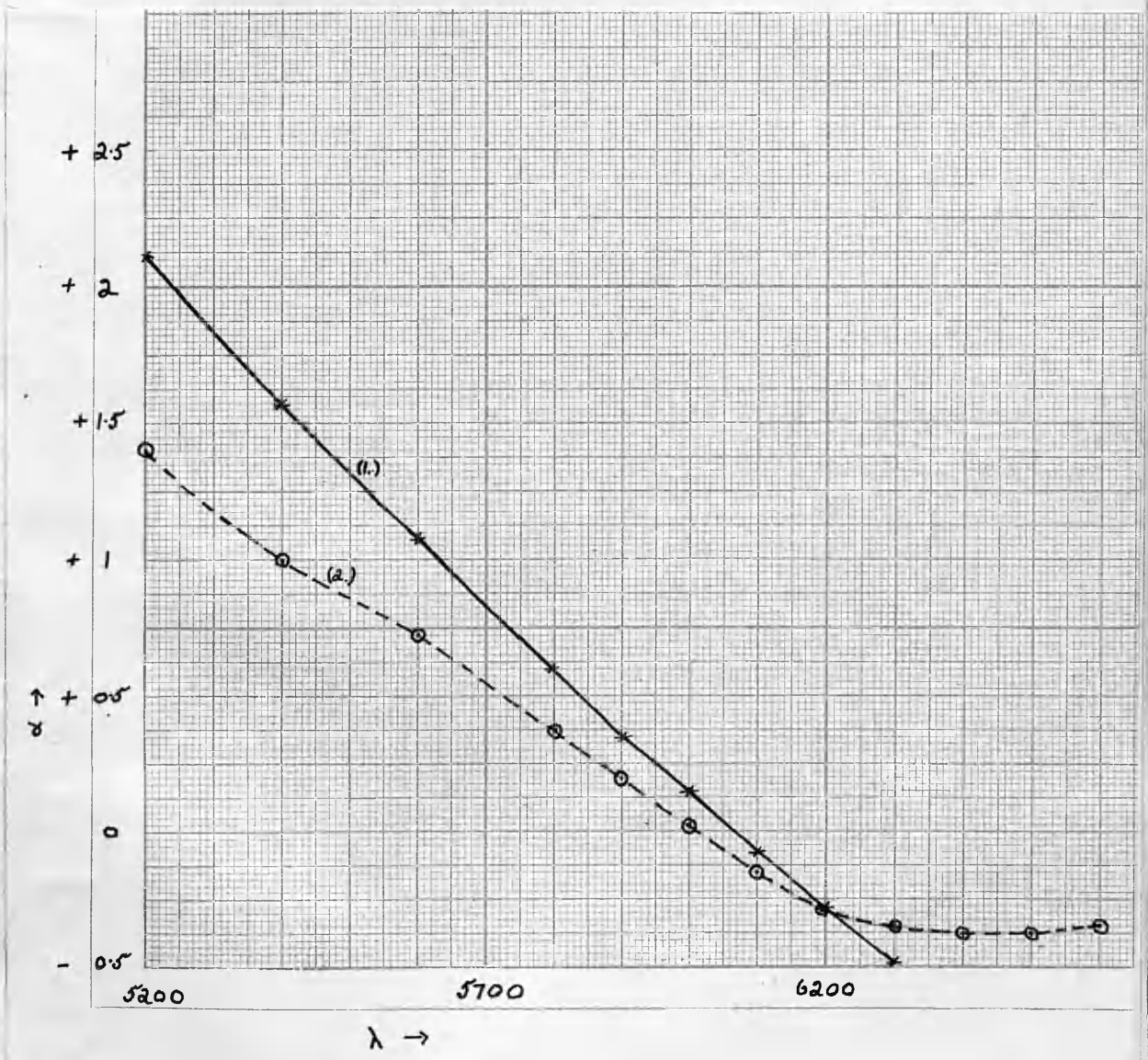
Rotation-Dispersion of Bis nitroso l-menthone at 56°.

λ	α	α'
5200	+2.11°	+1.40°
5400	+1.57°	+1.00°
5600	+1.08°	+0.72°
5800	+0.61°	+0.37°
5900	+0.35°	+0.19°
6000	+0.16°	+0.03°
6100	-0.08°	-0.16°
6200	-0.28°	-0.30°
6300	-0.49°	-0.36°
6400	-	-0.38°
6500	-	-0.38°
6600	-	-0.35°

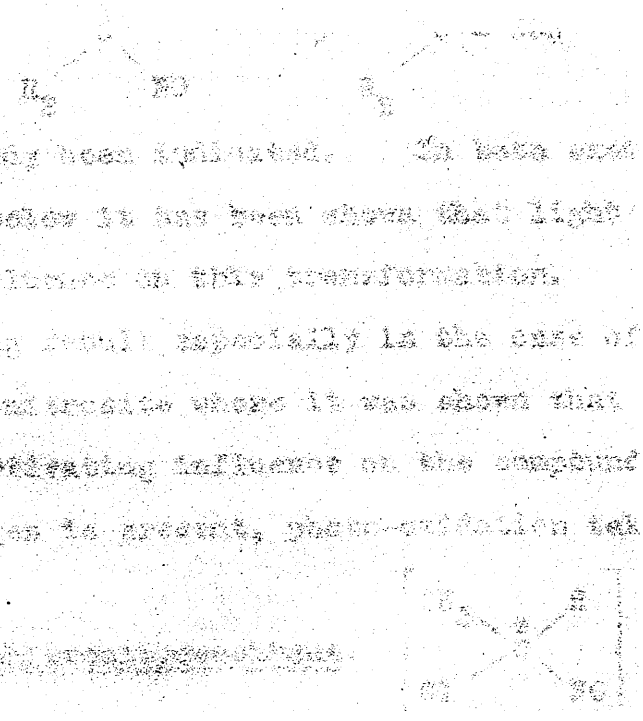
Graph No.3.

Rotation-Dispersion of Bis nitroso l-menthone.

Temperature 56°.



From these results there is little doubt as to the existence of a Cotton Effect associated with the absorption band in the red of the monomolecular form of bis nitroso l-menthone. However, the rapid diminution of rotation with time renders the compound definitely unsuitable for further work.

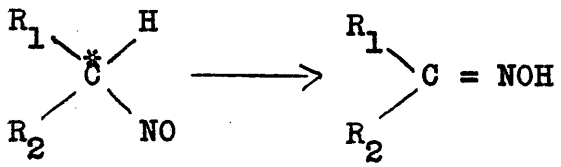


Part III. - The ACTION of NITROSYL CHLORIDE on n-HEXANE in PRESENCE of LIGHT.

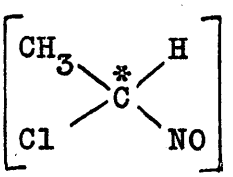
Introduction.

Secondary Nitroso Compounds.

The interest, from the point of view of asymmetric photochemical work, in the possible influence of light on the transformation of secondary nitroso compounds to the corresponding oximes,



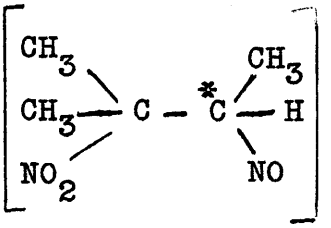
has already been indicated. In both examples considered below it has been shown that light has little or no influence on this transformation. This is a surprising result especially in the case of trimethylethylene nitrosite where it was shown that red light has an activating influence on the compound since, when oxygen is present, photo-oxidation takes place.

1. Monochloronitrosoethane. 

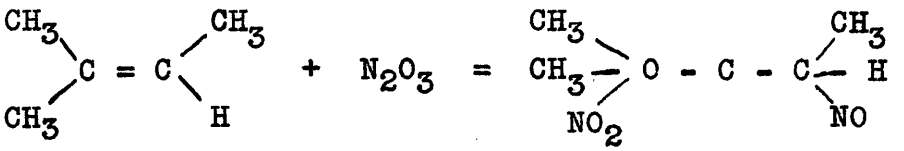
This compound was prepared by the action of chlorine on acetaldoxime and a good yield of the bimolecular form was obtained (25).

The white solid dissolved in all solvents tried to give deep blue solutions. Solutions in ether and glacial acid were decolorised at the same rate in the dark as when exposed to the light from a carbon arc. A solution in benzene after four hours' exposure to the light from a carbon arc was compared with a similar solution which had been kept in the dark. The solution which had been exposed to the light was very slightly greener in colour.

2. <u>Trimethylethylene nitrosite.</u>



This compound was prepared by passing the gases from the action of nitric acid on arsenious oxide into an ethereal solution of trimethylethylene, cooled in a freezing mixture (31).



The resulting blue ethereal solution was washed with water about twelve times, then dried over anhydrous sodium sulphate and the ether taken off under reduced pressure. The resulting violet blue oil on standing became green and deposited white crystals of the bi-molecular form, M.P. 75°. The nitrosite gave blue

solutions which were decomposed extremely slowly, in the absence of oxygen, by light. This photochemical action is so slow that it renders an attempt at an asymmetric photochemical decomposition with circularly polarised light impracticable.

These experiments now led to consideration of Lynn's 'secondary nitroso compounds', which, as already mentioned, were apparently converted into the corresponding oximes by the influence of light.

The work of Lynn.

The discovery of the action of light on solutions of nitrosyl chloride in n-heptane is due to Lynn (26). The reaction is apparently general for the paraffin hydrocarbons.

In a later paper by Lynn and Hilton (32) the results of investigation of the reaction involving n-heptane are given in detail and a brief summary of this paper is given below.

Crude nitrosyl chloride, made by heating aqua regia and so contaminated with chlorine, was used throughout since it was found by these authors that the crude reagent gave the same reaction products with n-heptane as did the pure.

A solution of crude nitrosyl chloride in n-heptane,

red-brown in colour, "was placed directly in the sunlight, the result being an immediate evolution of hydrogen chloride which continued for about one half hour. Sometimes samples appeared to be boiling vigorously. Accompanying the evolution of hydrogen chloride was a decided colour change from orange or reddish brown to green or blue, the shade depending on the degree of saturation. The colour usually obtained with highly saturated solutions was a verdant or emerald green. Also at this stage minute globules of an oil, usually light brown but sometimes dark, made their appearance. After the reaction had proceeded thus far, hydrogen chloride ceased to be given off so vigorously the colour gradually faded to either lighter shades of green or Copenhagen blue, the quantity of precipitated oil increased and finally the colour disappeared entirely an evident sign of complete reaction."

The precipitated oil was examined and found to be a mixture of oximes (presumably in the form of the hydrochlorides) principally butyronoxime $(C_3H_7)_2C = NOH$.

The authors assume that since hydrochloric acid gas is evolved at the beginning of the reaction the other product is a simple nitroso compound, producing the blue colour, and further that the disappearance of

the colour and precipitation of the brown oil is the result of this secondary nitroso compound changing over to the corresponding oxime by influence of the sunlight. The changes were therefore represented thus:-

$(CH_3CH_2CH_2)_2CH_2 + NOCl \longrightarrow (CH_3CH_2CH_2)_2CHNO + HCl$

$(CH_3CH_2CH_2)_2CHNO \longrightarrow (CH_3CH_2CH_2)_2C = NOH.$

It should be noted that Lynn confined his chemical investigation to the precipitated oil and did not attempt to isolate the nitroso compound from the reaction. Neither did he examine the supernatant liquid from which the oil had separated out. On these grounds principally, the conclusions arrived at by Lynn were considered to be rather speculative.

The principal nitroso compound from n-heptane does not contain an asymmetric carbon atom and it was decided, therefore, to investigate the action of nitrosyl chloride on n-hexane, in presence of light. By analogy with n-heptane, the following nitroso compounds should be formed in this case:-

$CH_3 - \overset{H}{\overset{|}{\overset{*}{C}}} - C_4H_9$, $C_2H_5 - \overset{H}{\overset{|}{\overset{*}{C}}} - C_3H_7$, and possibly $\left[C_5H_{12} - \overset{H}{\overset{|}{C}} - H \right]$
$\qquad\qquad\quad NO \qquad\qquad\qquad\quad NO \qquad\qquad\qquad\qquad\quad NO$

These compounds by the influence of light should give the corresponding oximes,

$CH_3 - \overset{\|}{C} - C_4H_9$, $C_2H_5 - \overset{\|}{C} - C_3H_7$, $\left[C_5H_{12}\overset{\|}{C} - H \right]$
$\qquad\quad NOH \qquad\qquad\qquad\quad NOH \qquad\qquad\qquad\quad NOH$

Preliminary Experiments.

The n-hexane used in all these experiments, unless otherwise stated, was obtained from the British Drug Houses, and gave B.P. 67 - 68°.

A small volume of n-hexane, in a boiling tube, was saturated with the gases from aqua regia. When completely saturated the solution was dark red in colour, and at this stage was placed in strong sunlight. The reaction proceeded almost exactly as described by Lynn for n-heptane. To begin with, streams of hydrogen chloride were given off and the solution changed in colour from dark red to green and then blue and a little light brown oil separated out. Finally the solution became colourless and the light brown oil became dark in colour.

A series of experiments, as described above, was then carried out to completion and the supernatant liquors, from which only a small quantity of oil had separated, were combined. It was deduced that the 'oximes' were mostly retained in solution. The hexane was therefore removed by distillation and the residue boiled up with dilute acid, to convert the 'oximes' to the corresponding 'ketones', and steam distilled. The oil obtained gave a small fraction boiling at 115 - 130°

and on warming above this temperature it charred. The fraction, 115 - 130°, gave $n_D^{20°}$ 1.4190 and did not form a semicarbazone. The refractive index of the ketones from n-hexane (after Lynn) is approximately $n_D^{20°}$ 1.4030, and the boiling points lie between 120° and 130°. From this it was concluded that the supernatant liquor did not contain the oximes, as had been expected, and also that the reaction is not as simple as Lynn had supposed.

The explanation of the above-described complication of the reaction was discovered when one of the experiments was stopped at the blue stage and the remaining nitrosyl chloride removed by blowing air through the solution. The resulting blue solution was concentrated in a vacuum desiccator and the dark blue liquid obtained was subjected to the influence of red light,

(1) In presence of oxygen.

(2) In absence of oxygen.

In the first case the blue colour disappeared fairly rapidly with no deposition of oil. In the second case the blue colour disappeared slowly with deposition of a black oil on the sides of the containing vessel. From this it was concluded that when oxygen is present the nitroso compounds are photo-oxidised and it was

probably the photo-oxidation products that were isolated from the supernatant liquor described above.

In the next section precautions for prevention of photo-oxidation will be described.

Experiments using crude nitrosyl chloride (from aqua regia).

From consideration of the course of the photochemical action it is evident that there are two definite stages in the change.

(1) Formation of the blue compounds.

(2) Destruction of the blue compounds.

Furthermore these two changes require different wave lengths of light. Thus, radiation other than red will cause the formation of the blue compounds, but red light is definitely necessary for the destruction of these blue compounds*. The latter fact was observed by Lynn but, peculiarly enough, he seemed to consider it rather a puzzling phenomenon.

Further experiments on the effective wave lengths of light, absorption spectra, etc. will be described later.

In order to investigate the possibility of isolating the blue compounds from the reaction mixture it is necessary to stop the photochemical action at the end

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* By the Grotthus-Draper law.

of the first stage. To accomplish this end the wave lengths of light effective in the destruction of the blue compounds were filtered off from the sunlight by means of a solution of copper sulphate. To be exact, the copper sulphate solution was used to cut out wave lengths greater than 6100A.

The apparatus used consisted of a series of glass tubes, about four feet in length, inside glass cylinders containing the copper sulphate solution. Each of the inside glass tubes was fitted with a cork and a lead-out tube dipping under water to absorb the hydrogen chloride given off. The tubes were filled with the hexane solution right up to the cork so that as soon as evolution of hydrogen chloride began the small amount of air present was driven out of the apparatus. This precaution is necessary to prevent any photo-oxidation.

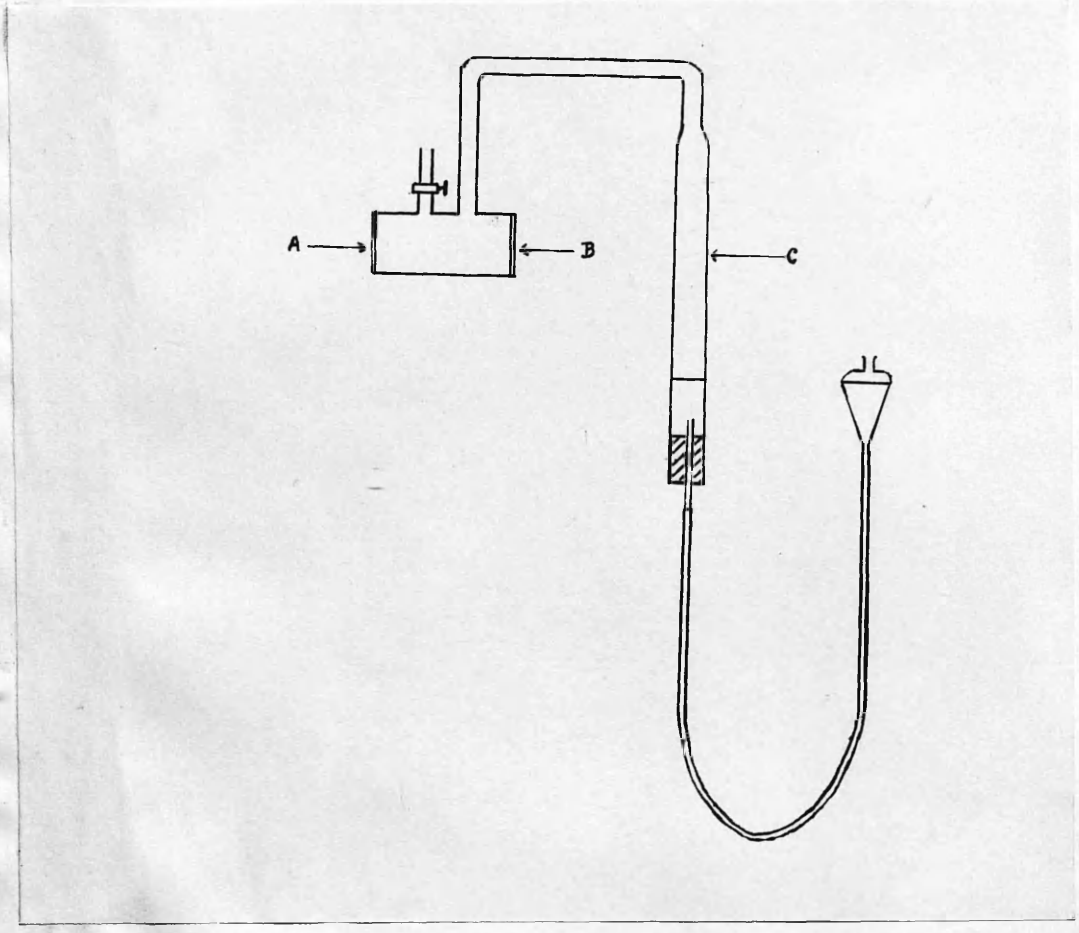
When the sunlight was strong the apparatus described above was set up out of doors.

During periods when sunlight was not available use was made of the radiation from a mercury vapour lamp. In this case the copper sulphate filters were found to be unnecessary on account of the fact that the red radiation from the mercury vapour lamp is very feeble. Here, however, it was found to be necessary to have water circulating round the glass tubes to

prevent warming up due to the heat from the lamp. After one hour of fairly bright sunlight the solutions of nitrosyl chloride in hexane had ceased to evolve hydrogen chloride and were blue in colour with only a little oil at the bottom of the tubes. At this stage the inside tubes were removed, the blue hexane solutions resaturated and the tubes replaced. This process was repeated twice, when the resulting solution was a fairly deep blue in colour.

About two litres of n-hexane were treated thus with the gases from aqua regia, the resulting blue solution decanted from the oil and air blown through it for some time to remove any unchanged nitrosyl chloride and most of the hydrogen chloride. An aqueous solution of sodium bicarbonate was then added and the mixture shaken up for several hours in an automatic shaker. The bicarbonate solution was then separated off, the blue hexane solution dried over anhydrous sodium sulphate and submitted to distillation under reduced pressure. The hexane distilled over first and was only faint blue in colour. Then a deep blue distillate was obtained and a small amount of a brown residue was left behind. The deep blue liquid, on redistillation twice, boiled at 34 - 36^{o} under a pressure of 14.8 m.m.

Photo-oxidation apparatus.



A and B - Glass windows sealed on with seccotine.

AB contains the blue solution.

C - Graduated tube filled with oxygen.

Photo-oxidation of the blue liquid, B.P. 34-36°/14.8 m.m.

A small quantity of the blue liquid was subjected to the influence of the light from a carbon arc in the photo-oxidation apparatus represented in the diagram on the opposite page, and the volume of oxygen absorbed was measured. It was found that for complete decolourisation, 0.24 gm. of the blue liquid absorbed 6.64 c.c. oxygen, measured at N.T.P. This value for the amount of oxygen absorbed provides a good check on the nitrogen content of samples of the blue liquid. (See later photo-oxidation data).

Analysis of the blue liquid, B.P. 34-36°/14.8 m.m.

A nitrogen estimation on the blue liquid gave 2% N, and a Carius estimation gave 29.2% Cl. These results, at first sight, are surprising, but on further consideration a likely explanation suggests itself. The nitrosyl chloride used was contaminated with chlorine and Michael and Turner (38) have shown that chlorine reacts readily with n-hexane, in the presence of sunlight, to give chloro derivatives, chiefly monochlorohexanes.

Monochlorohexanes contain 29.4% Cl.

Mononitrosohexanes contain 12.2% N.

From these figures it is seen that a combination of

these two compounds could be obtained to satisfy the analytical data of the blue liquid approximately if the presence of a small amount of dichlorohexanes is assumed.

In order to get over the difficulty of the formation of chlorohexanes it was decided to use pure nitrosyl chloride instead of the gases from aqua regia. Even using pure nitrosyl chloride, however, formation of some chlorohexanes is to be expected owing to the following decomposition

$$NOCl \longrightarrow NO + Cl$$

which, as Kistiakowsky (33) has shown, takes place by the influence of almost any wave length of light.

In the following section is given a detailed account of the investigation of the action of light on solutions of pure nitrosyl chloride in n-hexane.

Experiments using pure nitrosyl chloride.

Preparation of pure nitrosyl chloride.

Pure nitrosyl chloride was prepared by gently warming a mixture of pure nitrosyl sulphuric acid and an excess of dry common salt (27). It is necessary to have the apparatus for generation of the nitrosyl

chloride made entirely of glass, as cork and rubber are attacked very rapidly by the gas. The same applies to the apparatus for preparation of nitrosyl sulphuric acid.

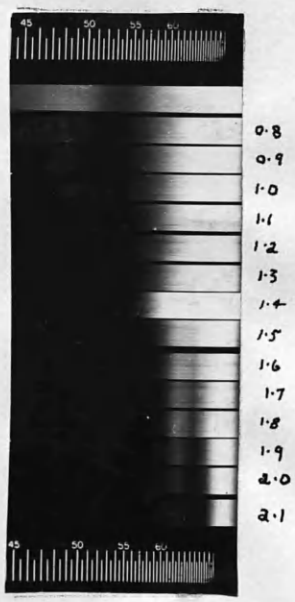
The nitrosyl sulphuric acid was prepared by passing sulphur dioxide rapidly into ice cooled fuming nitric acid, until brown fumes ceased to be evolved. A mass of crystals was deposited on standing over-night. These were filtered off rapidly through a sintered glass funnel. More solid was obtained by addition of glacial acetic acid to the mother liquor (35). The nitrosyl sulphuric acid was purified by washing with glacial acetic acid and then several times with carbon tetrachloride. The final pure white solid was kept in a desiccator over concentrated sulphuric acid (36).

The absorption spectra of a solution of pure nitrosyl chloride in n-hexane.

For the purpose of making up solutions of known concentration, for spectroscopic examination the nitrosyl chloride, prepared by the method described above, was liquefied in a freezing mixture and weighed directly into a flask containing the solvent. Examination of the absorption spectra in the visible was carried

out with a Hilger constant deviation spectroscope, which was first of all calibrated with a sodium flame. The source of light employed was a 100 c.p. Pointolite lamp. The solution used contained 0.54 gm. nitrosyl chloride in 42.57 gm. n-hexane. Two definite absorption bands with their heats at 6000A and 4780A approximately were found.

The very narrow band at 6000A approximately can be seen very well from the photograph given below. This photograph is a print from a plate taken with a spectrograph, using the above solution. The source of light was the Pointolite lamp, which is very rich in the red, and the plate used was panchromatic. Logarithms of thicknesses are marked in.



For measurements in the ultra violet the above solution was diluted ten times and an ordinary spectrograph employed. Absorption bands with their heads at approximately 3650A and 2900A were found.

The qualitative curve obtained from the absorption measurements with the visual spectroscope and the measurements in the ultra violet is given in Graph No.4.

It is interesting here to point out that Kistiakowsky (33) in his examination of the absorption spectra of gaseous nitrosyl chloride detected bands with their heads at approximately 5990A, 4690A, and 3300A. The first two bands correspond to the two bands in the visible at 6000A and 4790A for the solution in n-hexane.

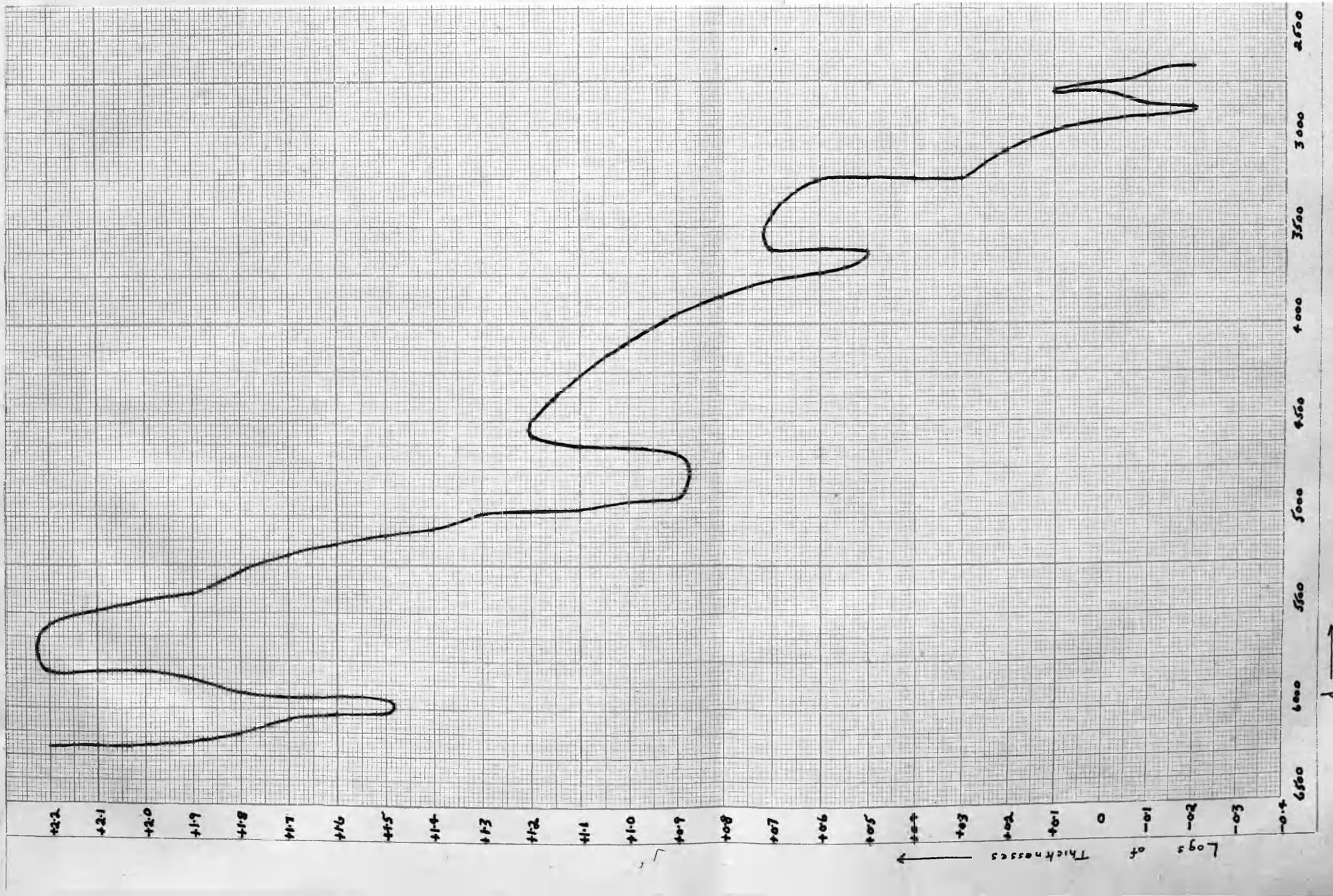
The wave lengths of light effective in the production of the blue compounds.

Lynn and Hilton (32) in their investigation of the photochemical action of nitrosyl chloride on n-heptane point out that formation of the blue colour takes place under the influence of sunlight or ultra violet light.

From consideration of the absorption spectra of solutions of nitrosyl chloride in n-hexane it is

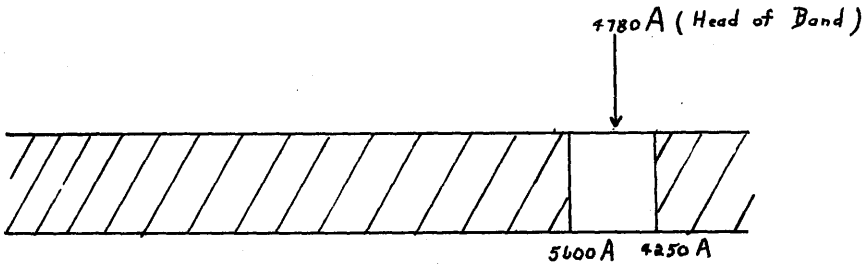
Graph No.4.

Qualitative absorption curve of a solution of pure nitrosyl chloride in n-hexane.

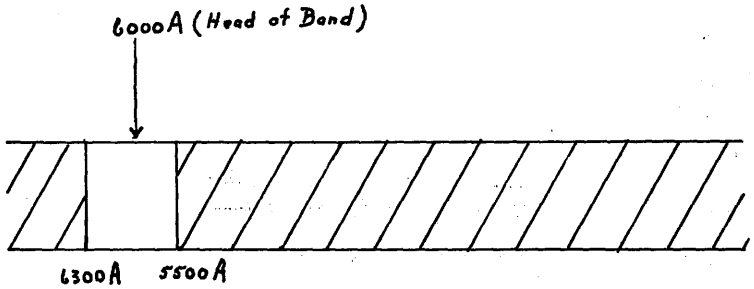


Test for effective wave lengths of light in production of the blue compounds.

1. Blue wave lengths.



2. Orange wave lengths.



interesting to enquire whether light corresponding to the absorption band in the blue (4780A) and the band in the orange (6000A) is effective in formation of the blue compounds from n-hexane.

In these experiments extra pure n-hexane was used since it was found that some samples of ordinary n-hexane gave a faint blue colour with nitrosyl chloride in the dark. This is probably due to traces of unsaturated hydrocarbons.

In order to see if the wave lengths of light corresponding to the absorption band in the blue are effective in the production of the blue colour a narrow band in the blue of the spectrum from the carbon arc was isolated by means of special filters. The narrow band isolated is represented in the diagram on page 47a. The filters used were:-

1. Blue filter, Wratten 45.
2. A layer of rosaniline in water.

A solution of nitrosyl chloride in n-hexane was exposed to this radiation for five hours. At this stage the nitrosyl chloride was removed by means of a current of air. The resulting solution was light blue in colour. A similar solution of nitrosyl chloride in n-hexane which had been kept in the dark was colourless on

removing the nitrosyl chloride.

The narrow band of the spectrum isolated to test the effectiveness of the orange radiation is illustrated on page 47a. The filters used were

1. Mercury yellow filter.
2. A layer of copper sulphate solution.

A faint blue solution was obtained after five hours' illumination with this radiation.

Thus it has been shown that light corresponding to both the absorption bands in the visible is effective in the first stage of the photochemical action. Ultra violet light is much more effective, however, as is seen very well from the speed at which the reaction proceeds on exposure to the radiation from a mercury vapour lamp.

The Photochemical action with pure nitrosyl chloride.

Investigation of the course of the photochemical action of pure nitrosyl chloride on n-hexane was undertaken in a similar manner to the investigation using crude nitrosyl chloride. That is to say, a large quantity of a solution of pure nitrosyl chloride in hexane was exposed to sunlight from which wave lengths greater than 6100A had been removed by copper sulphate

filters. The apparatus was the same as previously used and each solution was saturated and exposed to light four times. As before, the final solutions were light blue in colour and a little brown oil, presumably the decomposition product of the blue compounds, had separated out at the bottom of each tube.

An investigation into the exact nature of this oil was carried out and is described in the following section, while in a subsequent section an attempt to isolate the blue compounds from the blue mother liquor is described.

Examination of the brown oil.

The oil, which hereafter is referred to as oil A, was light brown in colour at first but on standing became dark brown. It smelled strongly of hydrogen chloride.

A sample of the oil was dissolved in water and neutralised by addition of barium carbonate. A top layer of oil separated out. The resulting mixture was steam distilled and the slightly yellow liquid produced was dried over anhydrous sodium sulphate and distilled under reduced pressure. The colourless distillate boiled at 79 - 82°/10 m.m., and gave $n_D^{20°}$ 1.4494. Trapesonzjanz (37) gives $n_D^{20°}$ 1.4464 for methyl n-butyl ketoxime.

Analysis of the liquid gave the following results:-

62.3% C ; 11.0% H.

The calculated figures for the oximes, C_6H_{12} = NOH, are

62.6% C ; 11.3% H.

A second portion of the oil was submitted to steam distillation without being neutralised. Such a procedure will convert oxime hydrochlorides to the corresponding ketones readily. The resulting fragrant liquid was dried over anhydrous sodium sulphate and distilled. The liquid which distilled over between 120° and 130° was colourless and gave $n_D^{19°}$ 1.4055. A sample of pure methyl n-butyl ketone (B.P. 126.5°) gave $n_D^{19°}$ 1.4030. On treatment with semicarbazide hydrochloride the liquid (B.P. 120 - 130°) yielded a semicarbazone, M.P. 113°, on crystallisation from alcohol. Analysis of the semicarbazone gave the following results:-

53.3% C ; 9.5% H ; 27.1% N.

The calculated figures for the semicarbazones from the ketones, $C_6H_{12}O$, are

53.5% C ; 9.55% H ; 26.8% N.

From these results it is evident that the brown

is a mixture of the hydrochlorides of oximes of formula $C_6H_{12} = NOH$.

The three possible oximes from n-hexane, with formula $C_6H_{12} = NOH$, are

$CH_3 - C(=NOH) - C_4H_9$, Methyl n-butyl ketoxime.

$C_2H_5 - C(=NOH) - C_3H_7$, ethyl n-propyl ketoxime.

$C_5H_{11} - C(=NOH) - H$, hexaldoxime.

The first two oximes give methyl n-butyl and ethyl n-propyl ketones, respectively, on hydrolysis and the third yields hexaldehyde. A complete analysis of the oxime hydrochloride mixture was carried out by the following method.

First of all the oximes were hydrolysed by acid steam distillation. The liquid produced, which may contain the two ketones and the aldehyde, was distilled and boiled over almost entirely between 120° and 130°. This boiling range embraces the boiling points of all suspected constituents. A sample of the liquid (B.P. 120 - 130°) was then subjected to the following test for hexaldehyde.

Michael and Turner have found that while hexaldehyde is readily oxidised by chromic acid solution

in the cold, both methyl n-butyl and ethyl n-propyl ketones are unaffected (38).

2 gm. of the liquid was treated with 25 c.c. of a solution of chromic acid made by dissolving 16 gm. potassium dichromate and 24 gm. sulphuric acid in water and making up to 200 c.c. The mixture was shaken up in a test tube frequently over a period of two days, then neutralised with caustic soda and steam distilled to remove unchanged ketones. The residue was acidified with phosphoric acid and steam distilled again. The distillate from this was then neutralised with ammonia and excess ammonia boiled off. The resulting solution gave no precipitate with silver nitrate indicating the absence of hexoic acid.

To confirm this result a little hexyl alcohol was shaken up with 25 c.c. of the chromic acid solution for the same time then neutralised and steam distilled. The distillate, after neutralising with ammonia and boiling off excess ammonia, gave a large precipitate of silver hexoate on addition of silver nitrate.

Thus it may be concluded that there is no aldehyde in the liquid B.P. 120 - 130°.

In order to find out the proportions of methyl

n-butyl and ethyl n-propyl ketones in this liquid a method, used successfully by Michael, was adopted (39).

Michael found that methyl n-butyl ketone forms a semicarbazone with acid semicarbazide phosphate, while ethyl n-propyl ketone does not.

The semicarbazide solution was made by dissolving 5 gm. of disodium hydrogen phosphate ($Na_2HPO_4 \cdot 12H_2O$), 2.5 gm. of 89% phosphoric acid and 3.6 gm. semicarbazide hydrochloride in a little water and diluting to a weight of 30 gm. Equal amounts (approximately 0.2 gm.) of pure methyl n-butyl ketone (B.P. 126.5°) and the mixture under investigation were weighed out into short thin test tubes and 3 c.c. of the semicarbazide solution added to each. The test tubes were shaken up frequently over a period of two days. The precipitates were then collected together in small sintered funnels, washed carefully with 3.5 c.c. water each and finally dried to constant weight in a vacuum desiccator. By comparison of the weight of semicarbazone from pure methyl n-butyl ketone with the amount from the mixture of methyl n-butyl and ethyl n-propyl ketones, the amount of methyl n-butyl ketone in the mixture was estimated.

It was found by this method that the liquid B.P. 120 - 130° contained approximately equal quantities of the two ketones. The figures varied from 50% - 55% methyl n-butyl ketone.

From these results it may be concluded that the brown oil consists of a mixture of the hydrochlorides of methyl n-butyl and ethyl n-propyl ketoximes in approximately equal quantities.

Examination of the blue solution.

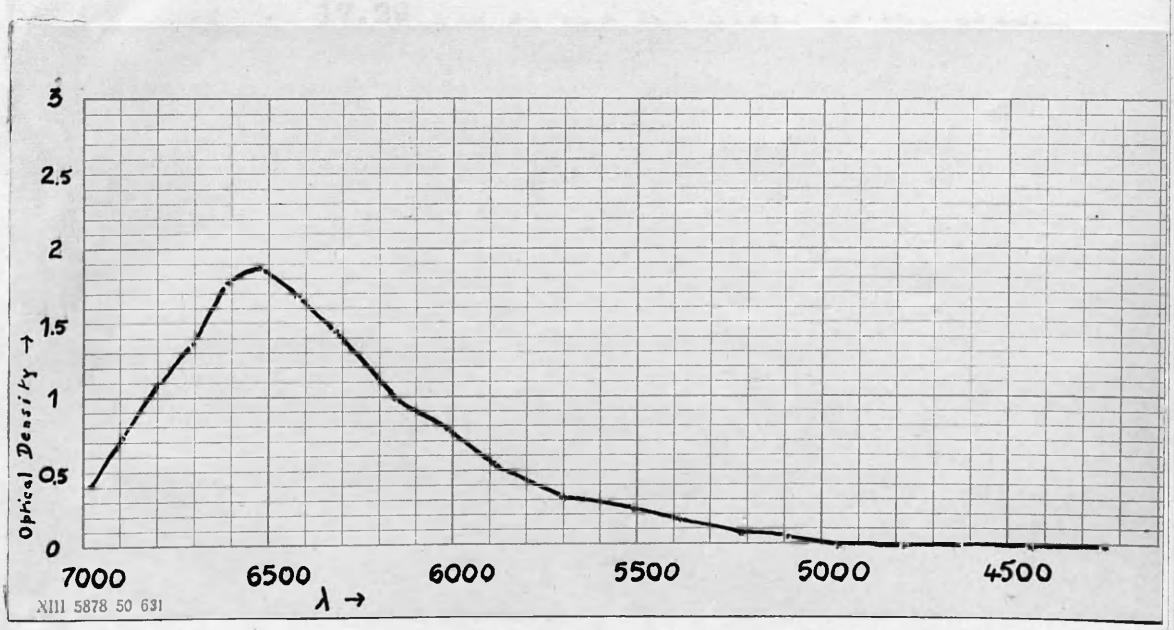
The blue solution, produced by the influence of light on solutions of pure nitrosyl chloride in hexane, was washed free from acid by shaking up for several hours with dilute sodium bicarbonate solution. It was then dried over anhydrous sodium sulphate and distilled under reduced pressure. The hexane which distilled over first was practically colourless and the blue distillate which was finally obtained, on redistillation several times, boiled at 39 - 42°/13 m.m. From one litre of hexane only a few c.c. of this liquid was obtained so its preparation is very tedious. Analysis of the liquid gave,

5.8% N ; 25% Cl.

The absorption spectra of a solution of this liquid in hexane was examined in the visible by means of a spectrodensograph. Graph No.5 shows wave length of light plotted against optical density. Length of solution = 2 cm. Concentration = 1.22 gm. in 100 c.c. The absorption band with its head at 6520A is characteristic

Graph No.5.

Absorption spectrum of a solution of the blue liquid from n-hexane.



of the nitroso group.

A photo-oxidation was then carried out with the liquid by the method previously described. It was found that 0.24 gm. of the blue liquid absorbed 17.29 c.c. of oxygen, measured at N.T.P.

0.24 gm. of the blue liquid (2% N), obtained by using crude nitrosyl chloride, absorbed 6.64 c.c. of oxygen at N.T.P.

The ratio of the volumes of oxygen absorbed by the liquids is $\frac{17.29}{6.64} = 2.6$, and the ratio of the nitrogen contents is $\frac{5.8}{2} = 2.9$.

This good agreement indicates that the total nitrogen content of the liquids is associated with the light sensitive nitroso compounds.

The high chlorine content of the blue liquid (25% Cl ; 5.8% N) is surprising and disagrees with the view that it consists of a mixture of secondary nitrosohexanes, $C_6H_{13}NO$ (12.2% N), and monochlorohexanes, $C_6H_{13}Cl$ (29.5% Cl).

This view also receives little support when the properties of the blue liquid are examined and comparison made with the properties of known secondary nitroso compounds.

As has already been mentioned, in the introduction to this thesis, generally speaking secondary nitroso

compounds cannot be isolated owing to the ease with which they change over to the corresponding isonitroso compounds (oximes). This is well born out from consideration of the researches of Tilden and Sudborough (40) and Ipatieff (41) on addition of nitrosyl chloride to compounds containing the ethylenic linkage, and the work of Bamberger (24) on oxidation of secondary alkylamines with Caro's acid.

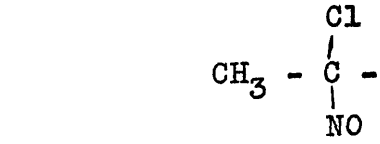
The most obvious exceptions to this rule are the nitroso compounds from trimethylethylene - trimethylethylene nitrosite, nitroso chloride and nitroso bromide. These secondary nitroso compounds are very stable in the bimolecular (white) form but in the monomolecular (blue) form they are readily converted to the isonitroso compounds by the influence of alkalis, heat, etc.

Examination of the blue liquid from hexane shows a decided difference in properties from secondary nitroso compounds. Thus it may be kept for several months in the dark without any apparent decomposition. It may also be distilled several times under reduced pressure at a temperature of 40° with little decomposition, and it is not decomposed by dilute alkalis.

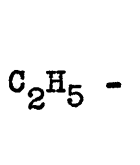
This stability of the blue liquid indicated that the blue compounds present are not secondary nitroso compounds. Further, the high chlorine content indicated that the nitroso compounds contain chlorine. So it seemed likely that the blue liquid is really a mixture of chloronitrosohexanes, $C_6H_{12}NOCl$ (9.6% N ; 23.7% Cl), in which the nitroso group is not attached to the same carbon as a hydrogen atom, and monochlorohexanes, $C_6H_{13}Cl$ (29.5% Cl). Such a mixture (approximately 50% of each) satisfies the analytical data.

The above supposition receives some confirmation from a molecular weight determination. The molecular weight corresponding to mixtures of nitrosohexanes and monochlorohexanes lies between 115 and 120, while the molecular weight corresponding to mixtures of chloronitrosohexanes and monochlorohexanes lies between 149 and 120. The actual molecular weight found from experiments on the lowering of the freezing point of benzene, by the blue liquid, was 136 which corresponds, within experimental error, to a mixture of equal amounts of monochlorohexanes and chloronitrosohexanes.

There are only two chloronitroso derivatives of n-hexane in which the nitroso group is not attached to the same carbon as a hydrogen atom. These are:-



ββ chloronitrosohexane



, γγ chloronitrosohexane.

These two compounds have been prepared by the action of nitrosyl chloride on methyl n-butyl and ethyl n-propyl ketoximes respectively, by Rheinboldt and Dewald (42). The boiling points given for the two compounds approximate very closely to the boiling point of the blue liquid from n-hexane.

For further confirmation that the blue liquid is a mixture of ββ and γγ chloronitrosohexanes and monochlorohexanes, the following experiment was undertaken.

Oxidation of the blue liquid with nitric acid.

Rheinboldt and Dewald (42) have found that chloronitroso compounds are oxidised by light and oxygen, or by nitric acid, to the corresponding chloronitro compounds. In the case of photo-oxidation the yield of chloronitro compounds was not as good as when nitric acid was used, indicating that photo-oxidation to chloronitro compounds is accompanied by other photochemical effects.

The boiling points of chloronitro compounds are considerably higher than the boiling points of the

corresponding chloronitroso compounds (and so also of the monochlorohexanes, in the case under consideration), so it was considered that, by oxidation of the blue liquid, a low boiling fraction of monochlorohexanes, unaffected by nitric acid, and a higher fraction of chloronitrohexanes, would be obtained. Analysis of these fractions would, of course, prove that the blue liquid has the constitution suggested.

10 gm. of the blue liquid was added to a mixture of 20 c.c. nitric acid (D. 1.42) and 10 c.c. glacial acetic acid. The resulting solution was gently warmed for about half an hour, when the blue colour had completely disappeared. The solution was then diluted with water and a yellow oil separated out. The oil was separated off, dissolved in ether and shaken up with dilute caustic soda solution, then with water several times and the ether solution finally dried over anhydrous sodium sulphate and distilled under reduced pressure. After the ether had been removed two fractions were obtained.

(1) B.P. 45 - 55°/15 m.m.,

(2) B.P. 73 - 77°/15 m.m.

A small amount of brown residue was left behind.

The first fraction gave a negative, while the second gave a positive nitrogen test.

On analysis the first fraction gave 29.7% Cl. Monochlorohexanes, $C_6H_{13}Cl$, contain 29.4% Cl.

The second fraction gave 22.0% Cl. Chloronitrohexanes, $C_6H_{12}NO_2Cl$, contain 21.4% Cl.

The high chlorine content in the second case is probably due to the presence of some monochlorohexanes, so this fraction was redistilled.

On redistillation the second fraction boiled over almost entirely at 79 - 80°/17 m.m. and on analysis gave 21.7% Cl. From this result, coupled with the analytical data previously given, it may be concluded that the blue liquid consists of a mixture of approximately 50% chloronitrosohexanes ($\beta\beta$ and $\gamma\gamma$ chloronitrosohexanes) and 50% monochlorohexanes.

Concerning the origin of the acid oil A, which has been shown to consist of a mixture of the hydrochlorides of methyl n-butyl and ethyl n-propyl ketoximes in approximately equal quantities, it seemed likely that it was produced by photochemical decomposition of the chloronitrosohexanes in absence of oxygen.

Rheinboldt and Dewald (42), although they observed photo-oxidation of chloronitroso compounds in general, do not record that such compounds are decomposed by light in absence of oxygen. It was therefore

considered necessary to subject the blue liquid (50% ββ and γγ chloronitrosohexanes, 50% monochlorohexanes) to the influence of light in absence of oxygen, in order to see if oximes are actually produced.

Photochemical Decomposition of the blue liquid in absence of oxygen.

1. In hexane solution.

A quantity of the blue liquid was dissolved in four times its volume of n-hexane. Several glass tubes were filled almost completely with this solution and sealed off carefully. These tubes, cooled by circulating water, were illuminated with light for several days, whereupon a black oil separated out and the blue colour of the solution disappeared slowly. When decomposition was complete the tubes were broken and the supernatant yellow liquid poured off. The viscous oil, which was left behind, smelled strongly of hydrogen chloride. This oil was washed out of tubes with water, the hydrochloric acid neutralised with barium carbonate and the mixture produced extracted with chloroform. The chloroform solution was dried over anhydrous sodium sulphate and distilled under reduced pressure. After the chloroform had distilled over a colourless distillate was obtained which, on redistillation, boiled at 80 - 82°/13 m.m. This liquid gave $n_D^{20°}$ 1.4493. (Methyl

n-butyl ketoxime gives $n_D^{20^\circ}$ 1.4464).

Thus it seems that, as suspected, by photochemical decomposition of ββ and γγ chloronitrosohexanes a quantity of methyl n-butyl and ethyl n-propyl ketoximes is produced.

In order to confirm this result it was considered necessary to carry out an analysis (carbon and hydrogen estimation) of the 'oximes' obtained. The yield of 'oximes' from the decomposition of the blue liquid, described above, is so small that it was decided to try solvents other than hexane to obtain a quantity for analysis.

First of all ethyl alcohol was used and in this case the reaction was found to proceed much faster, with very little charring, and no deposition of oil (oxime hydrochlorides being soluble in this solvent). The decomposition proceeded in a similar manner in solution in methyl alcohol and this solvent, on account of its lower boiling point, was used.

2. <u>In methyl alcohol solution.</u>

About 20 gm. of the blue liquid was dissolved in 30 c.c. of methyl alcohol and the solution, contained in sealed glass tubes, was exposed to bright sunlight. After an exposure of one day the blue colour had completely disappeared and the resulting solution was faint

brown in colour. The amount of hydrogen chloride liberated in one solution containing 4.78 gm. of the blue liquid was estimated by titration with caustic soda solution and found to be 0.59 gm. Calculating on the assumption that the total chlorine content of the chloronitroso compounds, in the mixture of 50% chloronitrosohexanes and 50% monochlorohexanes, is liberated as hydrogen chloride the weight of hydrogen chloride is 0.64 gm. This result will be discussed later.

The faint brown methyl alcohol solution, from the decomposition of the solution of the blue liquid, was distilled under reduced pressure. The acid oil left behind, after the methyl alcohol had been removed, was washed with a little hexane several times and the residue added to about 15 c.c. water, in which it was completely dissolved. This solution was then neutralised with barium carbonate and extracted with chloroform. The chloroform solution, after drying over anhydrous sodium sulphate, was distilled under reduced pressure. After the chloroform had been removed the residue distilled over almost entirely at 79 - 80°/11 mm. This liquid gave $n_D^{20°}$ 1.4494. These values for the

boiling point and refractive index correspond almost exactly to the values obtained for the oxime mixture from the acid oil A. On analysis the liquid gave

62.1% C ; 11.0% H.

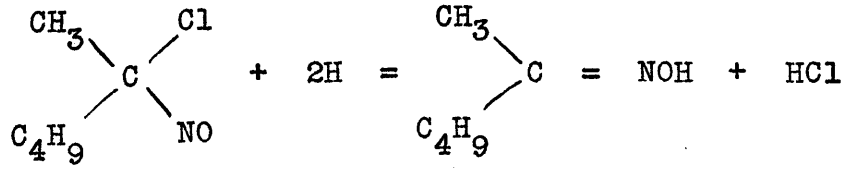
The oximes obtained from the acid oil A gave

62.3% C ; 11.0% H.

The calculated values from the oximes, $C_6H_{12}NOH$, are

62.6% C ; 11.3% H.

From this it may be concluded that, when solutions of ββ or γγ chloronitrosohexanes in hexane or methyl alcohol are acted upon by light in absence of oxygen, hydrogen chloride is produced together with a quantity of the corresponding oximes. Thus ββ chloronitrosohexane gives hydrogen chloride and methyl n-butyl ketoxime. This reaction is probably not quantitative although the amount of hydrogen chloride produced is almost theoretical. It was considered likely at first that the two hydrogen atoms necessary for the equation



are obtained from the solvent. This, however, receives no support from the fact that the chloronitroso compounds are decomposed by light, in absence of oxygen,

in solvents such as monochlorohexanes and hexane, which will not part with hydrogen readily; and also from the fact that when methyl alcohol was used as a solvent no trace of formaldehyde could be detected.

The main significance, however, of this photochemical action is that it explains the production of the acid oil A (oxime hydrochlorides) when solutions of nitrosyl chloride in n-hexane are exposed to white light, in the absence of oxygen.

Summary.

When a solution of nitrosyl chloride in n-hexane is exposed to white light, the red solution evolves hydrogen chloride, and changes in colour to green then blue and finally colourless, with deposition of a brown oil. The blue colour is due to ββ and γγ chloronitrosohexanes which are formed in the first stage of the reaction.

The mechanism of the first stage of the reaction is probably thus

$$C_6H_{14} + NOCl^* \longrightarrow \left[\begin{array}{l} C_6H_{13}NO \\ \text{secondary nitroso hexanes} \end{array}\right] + HCl$$

$$\downarrow$$

$$C_6H_{12} = NOH$$

$$\downarrow \; NOCl$$

$$C_6H_{12}NOCl$$

($\beta\beta$ and $\gamma\gamma$ chloronitroso-hexanes)

Chlorohexanes are also produced at this stage by the action on n-hexane of chlorine formed from nitrosyl chloride by the action of light, thus,

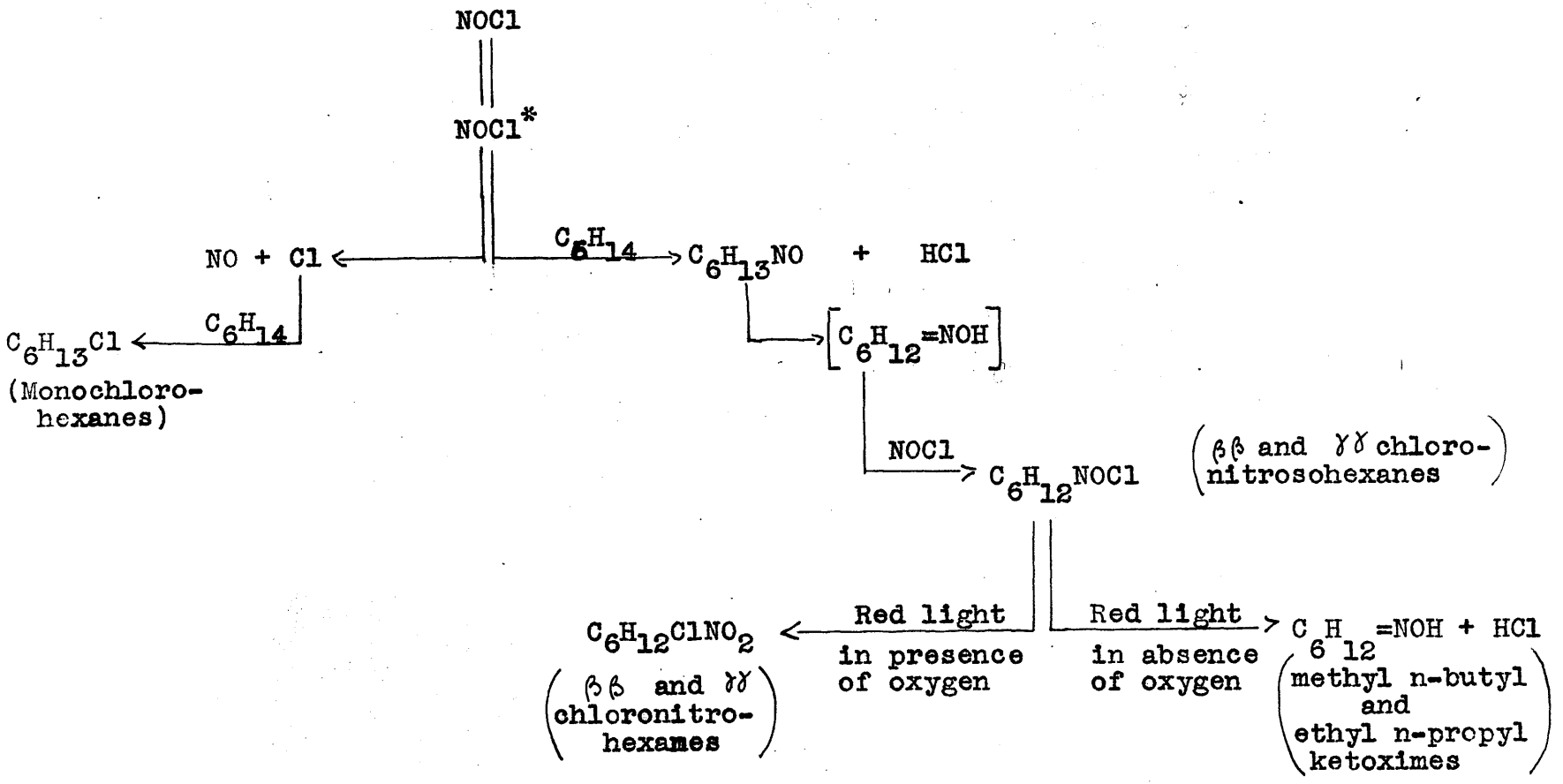
$$NOCl + \text{light} \longrightarrow NOCl^* \longrightarrow NO + Cl$$

The second stage of the reaction is decomposition of the chloronitroso compounds by red light with oxime hydrochlorides as the principal product, when no oxygen is present

$$\underset{\left(\begin{array}{c}\beta\beta \text{ and } \gamma\gamma \\ \text{chloronitrosohexanes}\end{array}\right)}{C_6H_{12}NOCl} \longrightarrow \underset{\left(\begin{array}{c}\text{methyl n-butyl and ethyl} \\ \text{n-propyl ketoxime} \\ \text{hydrochlorides}\end{array}\right)}{C_6H_{12} = NOH.HCl}$$

This is probably the stage at which the oil is deposited although some oxime hydrochlorides could be formed in the first stage, as may be seen from the equations previously given.

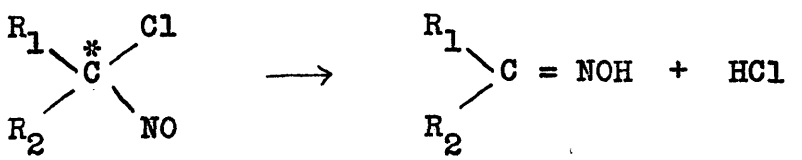
Since the oil which is deposited contains the two oxime hydrochlorides in equal amounts, it may be


NOCl
NOCl*
NO + Cl
C_6H_{14}
$C_6H_{13}NO$ + HCl
C_6H_{14}
$C_6H_{13}Cl$
(Monochloro-hexanes)
$[C_6H_{12}=NOH]$
NOCl
$C_6H_{12}NOCl$
(ββ and γγ chloro-nitrosohexanes)
Red light in presence of oxygen
Red light in absence of oxygen
$C_6H_{12}ClNO_2$
(ββ and γγ chloronitro-hexanes)
$C_6H_{12}=NOH$ + HCl
(methyl n-butyl and ethyl n-propyl ketoximes)

concluded that ββ and γγ chloronitrosohexanes are formed in approximately equal quantities. When oxygen is present photo-oxidation of the chloronitroso compounds will take place at the second stage. The complete photochemical action is represented diagramatically on the opposite page.

The research work described in this section entirely disproves the theory of Lynn as to the course of the action of light on solutions of nitrosyl chloride in paraffins, and a paper embodying the main results has been published (44).

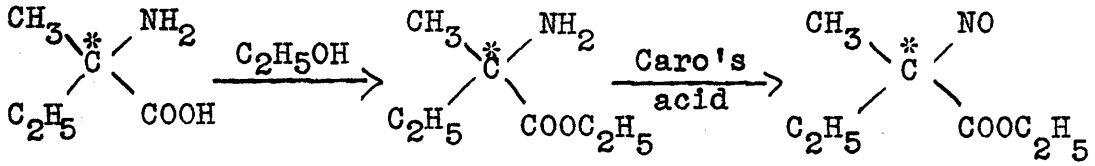
Other workers in these laboratories are investigating the possibilities of making use of chloronitroso compounds in asymmetric photochemical work in view of the discovery, in the course of this research work, of the photochemical decomposition of these compounds, in absence of oxygen, a decomposition which results in the destruction of the centre of asymmetry of the nitroso compound



Part IV. - PREPARATION of an OPTICALLY ACTIVE SIMPLE NITROSO COMPOUND.

The object of this preparation has already been indicated in the introduction to this thesis.

The compound selected was ethyl α-methyl-α-nitroso-n-butyrate and the general method of preparation is given by the following scheme,



Active iso-valin

Ethyl α-methyl-α-amino-n-butyrate

Ethyl α-methyl-α-nitroso-n-butyrate.

First of all a synthesis of the inactive nitroso compound was carried out, in order to find out if the amino group of the ester of isovalin is oxidised readily by Caro's acid to the nitroso group. This was successful and it was found that when neutral Caro's reagent was used about 20% yield of the nitroso compound was obtained.

The nitroso compound proved to be a beautifully crystalline solid melting at 65°C to give a blue liquid. Solutions of the compound were faint blue in the cold and on warming gently became deep blue. The compound

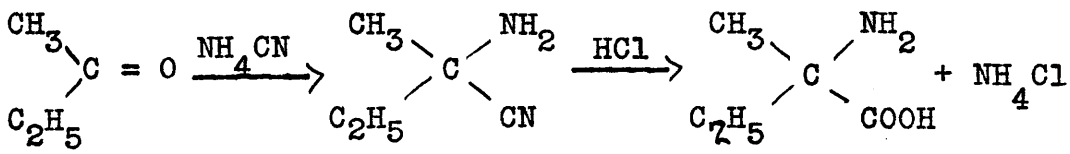
also appeared to be fairly stable since solutions could be warmed up frequently over a period of several days without any apparent decomposition, and the blue melt of the solid became white on solidification and remelted at the same temperature to give again a blue liquid.

A quantity of inactive isovalin was then prepared and resolved into its optical antipodes. The method of resolution, due to Gadamer (29), was fractional crystallisation of the Quinine Salt of formyl isovalin.

The preparation and resolution of inactive isovalin is now described.

Preparation of inactive isovalin.

This was carried out by the action of Ittner's 3% ammonium cyanide solution on methyl ethyl ketone and hydrolysis of the nitrile produced with concentrated hydrochloric acid (43).



The resulting hydrochloride of isovalin was separated from ammonium chloride by extraction with alcohol and ether. The residue, after evaporating the alcohol and ether, was freed from hydrogen chloride by prolonged boiling with litharge, the precipitated lead chloride being filtered off and the solution freed

from lead by precipitation with hydrogen sulphide. The pure amino acid was obtained from the final solution by evaporation until crystals appeared and then addition of alcohol.

500 gm. of pure isovalin was obtained by this method.

Formyl isovalin (28).

100 gm. of the pure amino acid, dried at 115°C, was heated in a boiling water bath with 244 gm. anhydrous formic acid for 3 hours. The formic acid was then removed by distillation under reduced pressure.

The above process was then repeated twice with the residue. The final residue was washed carefully with 300 c.c. ice cold water and recrystallised from nine times its weight of warm water. The resulting white solid gave M.P. 170 - 172°. The yield was 30%. The unconverted isovalin was recovered by evaporation and reformylated.

The formic acid recovered from the above process was dehydrated by several distillations over anhydrous copper sulphate at a pressure of 120 m.m., and used over again (45). The apparatus used for these distillations was made entirely of glass.

The Resolution.

The resolution was first of all carried out as

described by Gadamer (29) thus:-

20 gm. formyl isovalin was dissolved in 400 c.c. warm alcohol and 52.2 gm. Quinine, $[\alpha]_D$ -147°, added. The resulting solution was allowed to stand for two hours and the crystals, which had separated then (approximately 15 gm.) were filtered off quickly and recrystallised from about 120 c.c. alcohol, twice.

The resulting Quinine salt (approximately 7 gm.) was placed in a continuous extraction apparatus and 15 c.c. water and 7½ c.c. dilute sulphuric acid added. The mixture was extracted continuously for about three days. The formyl compound separated out from the ether extract and was crystallised from hot water. The active formyl isovalin obtained thus gave $[\alpha]_D$ -6.9° (Gadamer gives $[\alpha]_D$ -7.2°).

The isovalin was regenerated from the formyl compound by boiling with dilute hydrochloric acid, removing most of the hydrochloric acid by distillation under reduced pressure and finally removing the last traces by boiling with litharge. The amino acid was crystallised by addition of alcohol to a concentrated aqueous solution. The active isovalin obtained thus gave $[\alpha]_D$ +10.5°, (Gadamer gives $[\alpha]_D$ +10.75°) and the yield was 0.6 gm.

The yield of optically pure amino acid is so small that it was decided, for these experiments, to sacrifice high specific rotation for a better yield of a less optically pure compound.

Another resolution of the formyl compound was then carried out and this time half of the theoretical quantity of the Quinine salt was allowed to crystallise out. This quantity of crystals was recrystallised five times from absolute alcohol. The final amount of crystals (approximately 12 gm.) was treated as previously described to regenerate first of all the formyl compound and finally the amino acid. The yield of amino acid was about 1.5 gm. and the specific rotation $[\alpha]_D$ +8°.

The mother liquors from deposition of the first lots of crystals of the Quinine formyl isovalin were worked up to recover the negative amino acid.

Altogether seven resolutions as described above were carried out and the total amounts of active acid obtained are given below.

10 gm., $[\alpha]_D$ +8.2°,
15 gm., $[\alpha]_D$ -7.0°,
15 gm., $[\alpha]_D$ +2.2°.

Preparation of optically active Ethyl α-methyl α-amino n-butyrate.

10 gm. active isovalin $[\alpha]_D$ +8.2°, dried at 115°, was suspended in 75 c.c. absolute alcohol and dry hydrogen chloride passed in. In the course of about an hour the amino acid had gone into solution. The solution was then refluxed on a water bath for 3 hours, allowed to cool and the alcohol removed by distillation under reduced pressure. In the distillation under reduced pressure the temperature was not allowed to rise above 30°.

The viscous oil obtained was dissolved in a little water, cooled to -10° and a layer of ether added. 33% caustic soda solution was then added slowly with vigorous stirring, till exactly neutral. The ester was finally salted out of the aqueous layer by addition of potassium carbonate. The ether layer was then decanted off and dried carefully by allowing to stand over lime for about 12 hours. The ether solution was then distilled under reduced pressure and about 4.5 gm. ester, B.P. 65°/20 m.m., was obtained.

The specific rotation* of the ester was found to be $[\alpha]_D$ +5.5°, for the pure liquid.

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*Density taken as unity.

10 gm. of isovalin, $[\alpha]_D$ -7.0°, gave about 4.5 gm. ester, $[\alpha]_D$ -4.6°.

10 gm. of isovalin, $[\alpha]_D$ +2.2°, gave about 5 gm. ester, $[\alpha]_D$ +1.6°.

The rotation dispersion of the laevo ester was measured and found to be normal. The figures obtained for a layer of 0.6 decimetre of the pure liquid are given in Table (5).

α = Rotation.

λ = Wave length in Ängstöm units.

Graph No.6 shows rotation plotted against wave length.

Preparation of optically active Ethyl α-methyl-α-nitroso-n-butyrate.

The Caro's reagent was prepared by triturating 10 gm. potassium persulphate with 20 gm. concentrated sulphuric acid at 0°, allowing the mixture to stand for one hour at this temperature and then pouring it into 100 gm. ice. The solution produced was neutralised exactly with solid potassium carbonate and filtered.

1 gm. of ethyl α-methyl-α-amino n-butyrate, $[\alpha]_D$ +5.5°, was dissolved in 15 c.c. ether and added

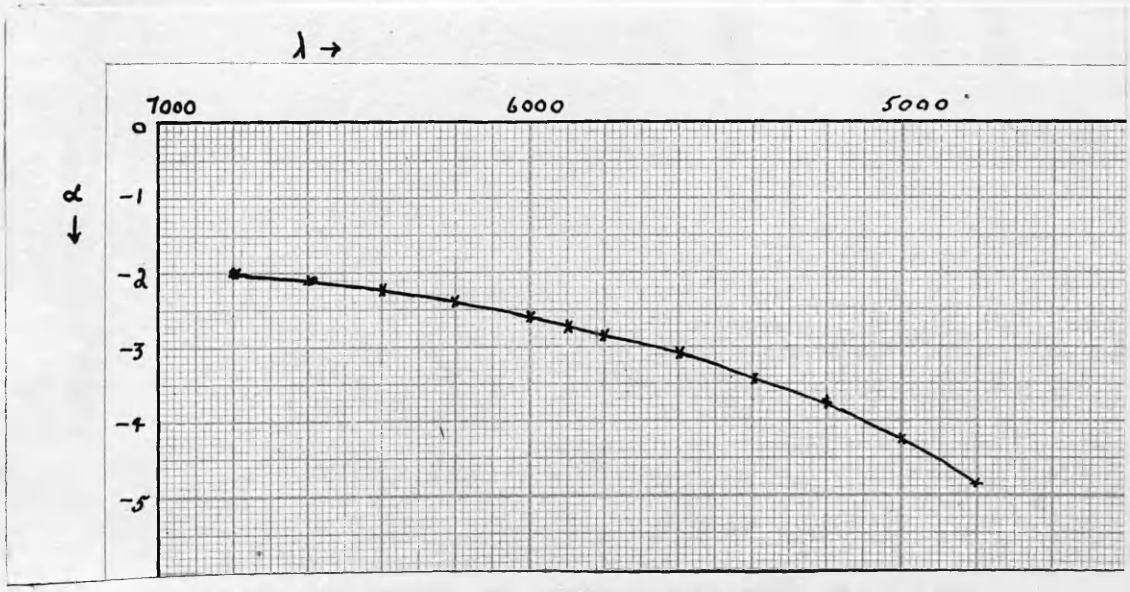
Table (5).

Rotation-Dispersion of laevo Ethyl α-methyl-α-amino-n-butyrate.

λ	α
5200	-3.71°
5400	-3.46°
5600	-3.11°
5800	-2.86°
5900	-2.75°
6000	-2.60°
6200	-2.41°
6400	-2.25°
6600	-2.09°
6800	-1.99°

Graph No.6.

Rotation-Dispersion of laevo ethyl ∝ -methyl -∝- amino-n-butyrate.



to 25 c.c. of the above solution of Caro's reagent, which had been cooled to 0°. The mixture was shaken up vigorously for five minutes, when the ether solution had become deep blue in colour. The blue ether solution was separated off, washed with sulphuric acid to remove unoxidised amine, then with water and dried over anhydrous sodium sulphate.

The layer of Caro's reagent which had been separated off was neutralised again with a little solid sodium carbonate, a further 25 c.c. Caro's reagent and 20 c.c. ether added to it and the whole shaken up for another 5 minutes. A further amount of blue ether solution was obtained.

The blue ether solutions were combined and evaporated in a vacuum desiccator. When the ether had almost entirely evaporated beautiful transparent crystals of the nitroso compound began to separate out. These were collected and dried on porous pot and gave M.P. 54 - 58°, which is 7 - 11° lower than for the inactive compound.

The yield from 1 gm. of the amine was 0.25 gm. nitroso compound.

The laevo ester was also converted to nitroso compound by this method.

The rotation of the active nitroso compound.

The rotation of a solution in ether of the

nitroso compound from the amino ester, $[\alpha]_D$ +5.5°, was measured and gave $[\alpha]_D$ -6.8°.
Length of solution in decimetres = l = 0.6.
Concentration of solution in gm. per 100 c.c. = c = 6.54.
Temperature = 20°.

The nitroso compound from the amino ester, $[\alpha]_D$ -4.6° gave $[\alpha]_D$ +6.1° in ether solution.
l = 0.6. c = 7.64. Temperature = 20°.

Rotation-Dispersion of the active nitroso compound.

1. Nitroso compound, $[\alpha]_D$ -6.8°.

Table (6) gives the results of measurement of rotation dispersion of the nitroso compound
l = 0.6. c = 6.54. Temperature = 20°.
These figures are represented graphically in Curve 1, Graph No.7.

From this curve it is seen that the dispersion is normal on the short wave side of 6000A. At 6000A the curve begins to flatten out and a definite minimum is seen at approximately 6600A, indicating the presence of a small Cotton Effect in this region.

2. Nitroso compound, $[\alpha]_D$ +6.1°.

Table (7) gives the results obtained for the dextro nitroso compound.

Table (6).

Rotation-Dispersion of laevo Ethyl α-methyl-α-nitroso-n-butyrate at 20°.

λ	α
5300	-0.48°
5500	-0.39°
5700	-0.32°
5900	-0.26°
6000	-0.23°
6100	-0.23°
6200	-0.22°
6300	-0.21°
6400	-0.18°
6500	-0.13°
6600	-0.12°
6700	-0.13°
6750	-0.18°
6800	-0.23°

Table (7).

Rotation-Dispersion of dextro Ethyl α-methyl-α-nitroso-n-butyrate at 19°.

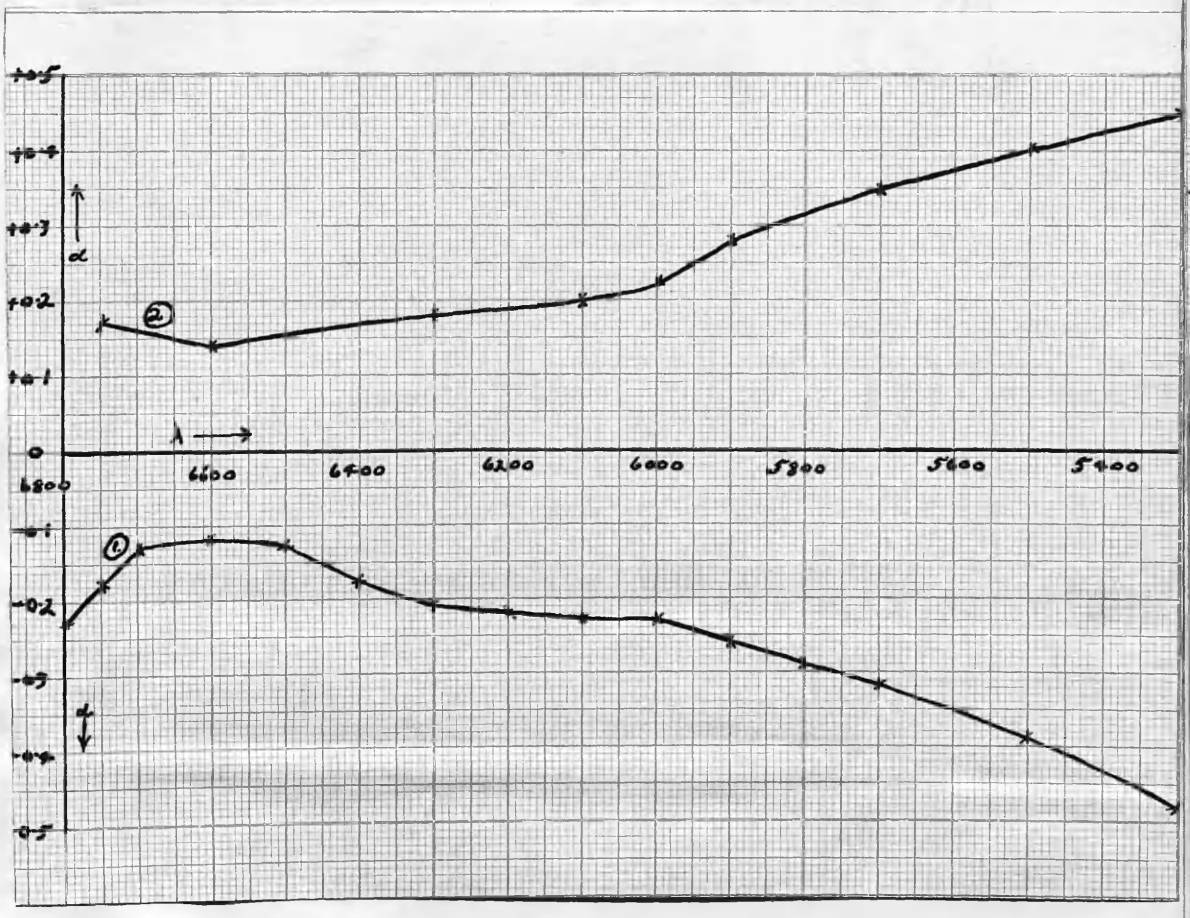
λ	α
5300	+0.45°
5500	+0.40°
5700	+0.35°
5900	+0.28°
6000	+0.22°
6100	+0.20°
6300	+0.18°
6600	+0.14°
6750	+0.16°

Graph No.7.

Rotation-Dispersion of ethyl ∝-methyl-∝-nitroso-n-butyrate.

(1) Laevo at 20°.

(2) Dextro at 19°.



l = 0.6. c = 7.64. Temperature = 19°.

These figures are represented graphically in Curve 2, Graph No.7.

The anomaly in the dispersion is not so prominent in this curve but the agreement with Curve 1 is practically within experimental error.

Rotation-dispersion measurements were now taken at different temperatures. The anomaly in the dispersion curve is due to the monomolecular blue form of the nitroso compound and so should become more accentuated on warming, when the solution becomes more blue and less accentuated on cooling.

Table (8) gives the results obtained at 0° for a solution of the laevo nitroso compound

l = 0.6. c = 6.51.

These results are plotted in Graph No.8. From this curve it is seen that the anomaly has almost disappeared.

For measurements at higher temperatures, when strong absorption in the red begins, it is necessary to use a thinner layer of solution if readings are to be possible at the red end of the spectrum. This, unfortunately, results in a diminution of actual rotation to be measured.

Measurements with a layer of 0.25 decimetre of a solution of 0.364 gm. of nitroso compound, $[\alpha]_D$ +6.1°,

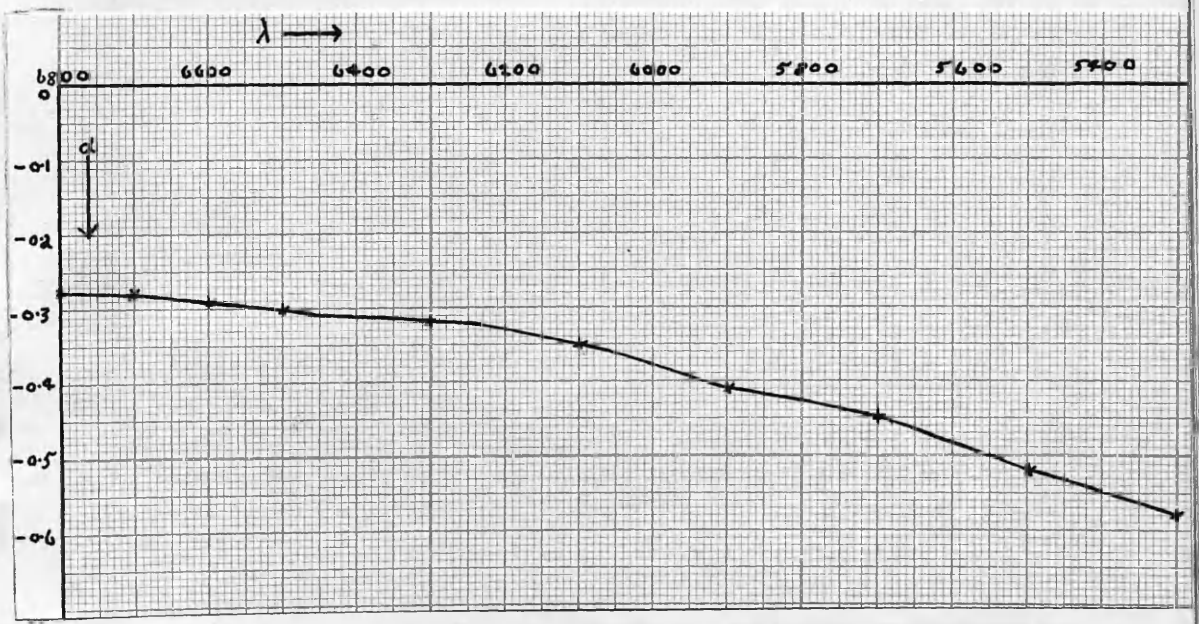
Table (8).

Rotation-Dispersion of laevo Ethyl α-methyl-α-nitroso-n-butyrate at 0°.

λ	α
5300	-0.58°
5500	-0.52°
5700	-0.45°
5900	-0.41°
6100	-0.35°
6300	-0.32°
6500	-0.31°
6600	-0.29°
6700	-0.28°
6800	-0.28°

Graph No.8.

Rotation-Dispersion of laevo ethyl α-methyl-α-nitroso-n-butyrate at 0^{o}.



in 5 c.c. benzene, were taken at 30°, 40° and 50°. At 50° it was just possible to see through the solution at 6700A.

The readings are given in Table (9); Graph No.9; Curves 1, 2 and 3 show rotation readings plotted against wave length, at 30°, 40° and 50° respectively.

The anomaly in the dispersion curve was not so pronounced at these higher temperatures. This may be accounted for by the low value of the actual rotation at these temperatures, due primarily to the short length of solution which had to be used and also to a certain amount of decomposition of the nitroso compound.

A test for circular dichroism was made with the solution at 50° but none could be detected.

Summary.

It has been found possible, by the method described, to prepare an optically active simple nitroso compound, ethyl ∝-methyl-∝-nitroso-n-butyrate.

The specific rotation of the nitroso compound prepared from dextro isovalin, which was approximately 75% optically pure, was $[\alpha]_D^{20^\circ}$ -6.8° in solution in ether. This gives $[\alpha]_D^{20^\circ}$ -9.1°, for the optically

Table (9).

Rotation-Dispersion of dextro Ethyl α-methyl-α-nitroso-n-butyrate at 30°, 40° and 50°.

λ	α (Temp. 30°)	α (Temp. 40°)	α (Temp. 50°)
5500	-	-	+0.12°
5700	+0.32°	+0.24°	-
5800	-	-	+0.08°
5900	+0.22°	+0.20°	-
6000	-	-	+0.06°
6100	+0.17°	+0.17°	-
6200	-	+0.15°	+0.06°
6300	-	-	+0.04°
6400	+0.12°	+0.12°	+0.04°
6500	-	-	-
6600	+0.12°	+0.12°	+0.04°
6700	-	-	-
6800	+0.13°	+0.12°	-
6900	+0.14°	+0.12°	-

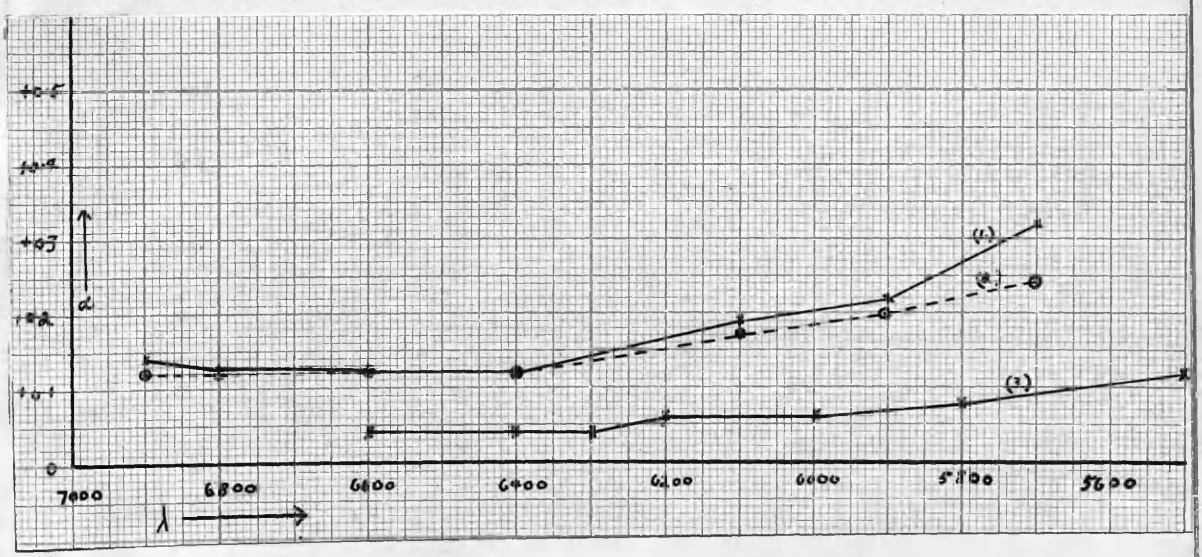
Graph No.9.

Rotation-Dispersion of dextro ethyl-α-methyl-α-nitroso-n-butyrate.

(1) Temperature 30°.

(2) Temperature 40°.

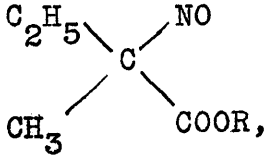
(3) Temperature 50°.



pure nitroso compound, assuming that there is no racemisation in the process of formation. It should be noted that this specific rotation is really a combination of two factors, first, the specific rotation of the bimolecular compound and secondly that of the monomolecular compound, since the solutions at this temperature were light blue in colour.

No circular dichroism was detected in solutions of the nitroso compound at temperatures up to 50° but a slight anomaly in the rotation dispersion curve, at 20°, was found in the region of the absorption band in the red*, indicating a small Cotton Effect.

The magnitude of the rotation and circular dichroism associated with the active form of Ethyl α-methyl-α-nitroso-n-butyrate is too small to make this compound valuable from the point of view of asymmetric photochemical work. However, other members of the series,



to which the above compound belongs, may show larger effects and these other members may be obtained in the optically active form by the method described in the foregoing section.

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*The head of this band was found to be at 6800A approximately.

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